

AD-A086 579 ENERGY RESEARCH CORP DANBURY CONN  
AQUEOUS TRIFLUOROMETHANESULFONIC ACID FUEL CELLS. (U)  
DEC 79 M GEORGE  
UNCLASSIFIED ERC-6184-I

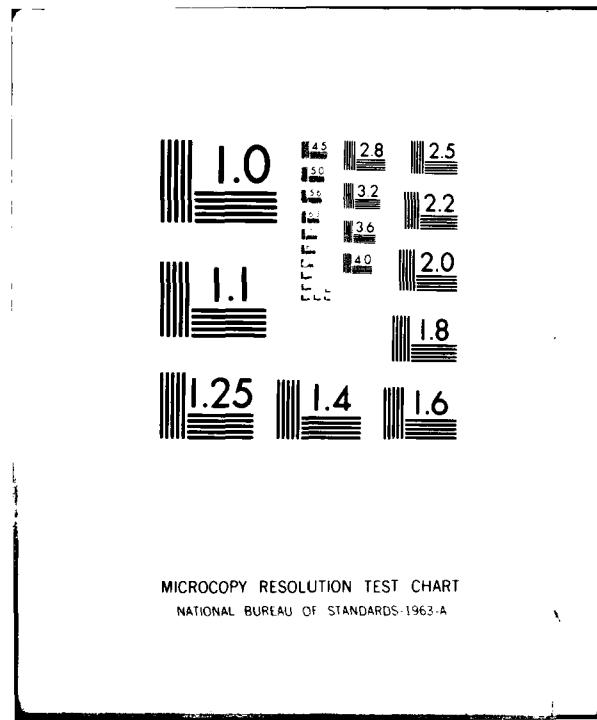
F/0 10/2

DAAK70-78-C-0103

ML

1 OF 1  
AD-A086 579

END  
DATE 12-19-80  
8-80  
DTIC



REV 86579

LEVEL  
X

ERC-6154-I

(12)

AQUEOUS TRIFLUOROMETHANESULFONIC ACID FUEL CELLS

INTERIM TECHNICAL REPORT

December 1979

by

Michael George

US ARMY MOBILITY EQUIPMENT  
RESEARCH & DEVELOPMENT COMMAND  
Fort Belvoir, VA 22060

DTIC  
SELECTED

JUL 7 1980

C

Contract No. DAAK70-78-C-0103

This document has been approved for public  
release and sale; its distribution is unlimited

ENERGY RESEARCH CORPORATION  
3 Great Pasture Road  
Danbury, CT 06810

DDC FILE COPY

80 7 2 032

## N O T I C E S

### Disclaimers

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

The citation of trade names and names of manufacturers in this report is not to be construed as official Government indorsement or approval of commercial products or services referenced herein.

### Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ERC-6154-I	2. GOVT ACCESSION NO. <i>AD-A086 579</i>	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) AQUEOUS TRIFLUOROMETHANESULFONIC ACID FUEL CELLS		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Progress June 1978 - Aug 1979
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Michael George	8. CONTRACT OR GRANT NUMBER(s) DAAK70-78-C-0103	
9. PERFORMING ORGANIZATION NAME AND ADDRESS ENERGY RESEARCH CORPORATION 3 Great Pasture Road Danbury, CT 06810	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS DEFENSE LOGISTICS AGENCY, DCASMA, Bridgeport 500 South Main Street Stratford, CT 06497	12. REPORT DATE December 1979	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) U. S. ARMY MOBILITY EQUIPMENT RESEARCH & DEVELOPMENT COMMAND Fort Belvoir, VA 22060	13. NUMBER OF PAGES 39	
	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  This document has been approved for public release and sale, its distribution is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  Approved for Public Release, Distribution Unlimited		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) TRIFLUOROMETHANESULFONIC ACID FUEL CELLS ELECTROCATALYSTS OXYGEN REDUCTION ACTIVITY COEFFICIENTS		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Subscale hydrogen-air fuel cells were successfully operated with 6M TFMSA as the electrolyte at temperatures as high as 60°C. The fuel cell performance was enhanced over similarly loaded electrodes in H <sub>3</sub> PO <sub>4</sub> due to the apparent improved kinetics for the oxygen reduction reaction. A variety of unsupported and supported Pt electrocatalysts could be effectively utilized. TFMSA fuel cells could be operated stably for periods as long as 3000 hours if water balance was maintained. Activity coefficients calculated by the van Laar equations were utilized to predict water partial pressures of dilute TFMSA solutions.		

*381267*

ENERGY RESEARCH CORPORATION

TABLE OF CONTENTS

	<u>Page No.</u>
1.0 INTRODUCTION	1
2.0 TECHNICAL APPROACH	3
2.1 <u>Analytical Procedures</u>	3
2.1.1 Water Management Problem	3
2.1.2 Identification of Optimum Concentration	11
2.2 <u>Experimental Procedures</u>	18
2.2.1 Electrode Fabrication	18
2.2.2 Fuel Cell Assembly and Testing	19
2.3 <u>Results and Discussion</u>	21
3.0 CONCLUSIONS	37
4.0 RECOMMENDATIONS FOR FUTURE WORK	38
REFERENCES CITED	39

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DDC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	<input type="checkbox"/>
By _____	
Distribution _____	
Availability _____	
Dist	Available or special
A	

**ENERGY RESEARCH CORPORATION**

**LIST OF FIGURES**

<u>Figure No.</u>		<u>Page No.</u>
1	Vapor Pressures of Pure TFMSA	7
2	Phase Diagram of TFMSA-Water System at 60°C	10
3	Experimentally Obtained Vapor Pressures of of TFMSA Solutions	12
4	Vapor Pressures of TFMSA-Water Solutions at 60°C	13
5	Conductivities of TFMSA-Water Solutions	15
6	Contact Angles of TFMSA-Water Solutions on PTFE	16
7	Performance of Pt Black Electrodes with 2 mg/cm <sup>2</sup> Pt Loading	23
8	Performance of Pt Black Electrodes with 4 mg/cm <sup>2</sup> Pt Loading	24
9	Tafel Plot of 4 mg/cm <sup>2</sup> Pt Black Electrode	25
10	Endurance of Pt Black Electrodes	27
11	Endurance of Pt Black Electrodes with Dry Air	29
12	Endurance of Pt Black Electrodes with Presaturated Air	30
13	Performance of Pt on Kocite Electrodes	32
14	Comparison of Electrode Performance in TFMSA and H <sub>3</sub> PO <sub>4</sub>	33
15	Endurance of Pt on Kocite Electrodes	34
16	Performance of Pt on Carbon Electrodes	35
17	Endurance of Pt on Carbon Black Electrodes	36

**LIST OF TABLES**

<u>Table No.</u>		<u>Page No.</u>
1	Activity Coefficients and Partial Pressures at 60°C	8
2	Properties of TFMSA-Water Solutions at 60°C	17

1.0 INTRODUCTION

This is an Interim Technical Progress Report for Contract No. DAAK70-78-C-0103 entitled Aqueous Trifluoromethanesulfonic Acid Fuel Cells. The work, performed between June 1978 and August 1979, is summarized within this report.

Phosphoric acid, currently recognized as the most practical acid fuel cell electrolyte, is preferred since it allows fuel cells to operate at moderately high temperatures (in the range of 150 to 200°C). At these temperatures, phosphoric acid resists decomposition and exhibits low volatility characteristics. Although it is an exceptionally stable electrolyte, phosphoric acid possesses other characteristics which hinder its application in an actual fuel cell. It is not a particularly strong acid; therefore it has less ionic conductivity than more fully ionized electrolytes such as sulfuric acid. In addition, the anion of phosphoric acid is believed to readily adsorb on noble metal catalysts which impedes the electrochemical kinetics in the fuel cell. Since the acid fuel cell is nearly always controlled by the rate of oxygen reduction reaction, this suspected poisoning effect associated with phosphoric acid tends to severely limit its efficiency in the fuel cell.

Various solutions (including some common acids such as sulfuric and perchloric) which have less tendency to restrict the kinetics of the electrochemical reactions have been proposed for use in fuel cells. Many of these acids, however, are susceptible to decomposition, even at moderate fuel cell temperatures. In 1973, a promising, new family of potential fuel cell electrolytes was revealed: the perfluoroalkane sulfonic acids.<sup>1</sup> Subsequent studies have suggested that the monohydrate of trifluoromethanesulfonic acid (TFMSA) would be a viable fuel cell electrolyte since its oxygen reduction reaction was considerably more enhanced than phosphoric acid's.<sup>2</sup>

TFMSA, commonly referred to as triflic acid, is sometimes described as one of the strongest known acids. In the pure form, however, it is reported to have an extremely low ionic conductivity.<sup>5</sup> The boiling point of the pure acid is only 162°C which indicates that the pure acid would readily vaporize at moderate fuel cell temperatures. The monohydrate of TFMSA was initially attractive since it appeared to be a constant boiling point mixture with a normal boiling point of 217°C. This would suggest that the monohydrate was a maximum boiling point azeotrope and subsequently the composition with the lowest total vapor pressure.

An extensive evaluation of the merits of TFMSA monohydrate

ENERGY RESEARCH CORPORATION

was conducted during Contract No. DAAK02-75-C-0045, entitled "New Materials for Fluorosulfonic Acid Electrolyte Fuel Cells." During initial evaluation of the monohydrate at moderate fuel cell temperatures, acid loss from operating cells was very evident. White fumes, visible in the cell exit gas streams, suggested that the partial pressure of the pure acid was significant with the monohydrate composition. Since the monohydrate was an azeotropic mixture, the vapor phase in equilibrium with the monohydrate solution would also have the monohydrate composition. Thus the partial pressures of the pure acid and water should be in a one-to-one ratio and each equivalent to 50% of the total vapor pressure. Although the monohydrate had the lowest total vapor pressure, it was not the composition with the lowest acid partial pressure.

The monohydrate was also observed to wet PTFE, the common acid fuel cell electrode binder and wetproofing agent. This severely complicated the fabrication of a non-flooding electrode structure. Cells containing the monohydrate also exhibited abnormally high internal resistances which implied the ionic conductivity of the azeotropic composition was relatively poor. Conductivity of the monohydrate was later shown to be less than  $.02 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $40^\circ\text{C}$ .<sup>3</sup> This value compares unfavorably with the ionic conductivity of 100% phosphoric acid at  $160^\circ\text{C}$  ( $.53 \text{ ohm}^{-1} \text{ cm}^{-1}$ ).

Since the monohydrate of triflic acid was not feasible within a real fuel cell, subsequent emphasis was placed on evaluating aqueous TFMSA solutions. Aqueous solutions in which the mole fraction of TFMSA was less than about .20 did not appear to have the same limitations as the monohydrate. The dilute solutions did not have the tendency to wet PTFE, and also possessed ionic conductivities at  $40^\circ\text{C}$ , roughly equivalent to concentrated phosphoric acid at  $160^\circ\text{C}$ . In addition, the acid partial pressures were inherently reduced with the dilute TFMSA solutions, eliminating any short-term acid loss problems.

During Contract DAAK02-75-C-0045, considerable progress was made in operating Pt black type electrodes in aqueous TFMSA fuel cells at ambient temperatures. It was generally acknowledged that the fuel cell performance was enhanced over similarly loaded electrodes operating in phosphoric acid cells at much higher temperatures. Although the potential for aqueous TFMSA fuel cells was demonstrated, many problem areas also became evident. The TFMSA fuel cell was not as inherently stable as the phosphoric acid fuel cell. Also there was a general inability to effectively operate cells either at higher than ambient temperature or with supported catalyst type electrodes.

Contract DAAK-70-78-C-0103 represents an effort to overcome

**ENERGY RESEARCH CORPORATION**

some of the difficulties previously identified with aqueous TFMSA fuel cells. The major objectives are:

- Demonstration of stable performance by effective water management within continually operating cells.
- Demonstration of stable performance at higher than ambient temperature.
- Improved performance with supported catalyst type electrodes.
- Identification of optimum electrolyte concentration levels.

2.0            **TECHNICAL APPROACH**

2.1            Analytical Procedures

2.1.1          Water Management Problem

Although very promising initial performance levels were demonstrated for aqueous triflic acid fuel cells during Contract DAAK02-75-C-0045, difficulties were encountered in maintaining cell stability for long operational periods. A trial and error approach was tried regarding water management. Since continually functioning cells produce significant amounts of product water at normal current densities, operation at ambient temperatures necessitated passage of abnormally high air flows. Decay was evident in all cells although, in some cases, initial performance could be restored by changing the cell operating parameters. Much of the cell decay appeared to be related to increased electrode diffusional losses (flooding) as increased oxygen gains generally occurred. The electrode flooding problem probably was created by electrolyte concentration changes. It could be rationalized that electrode flooding would occur if the original acid was either diluted or concentrated to any degree. Acid dilution would greatly increase the volume of electrolyte present in the electrode structure while acid concentration would adversely affect the wetting characteristics of the electrolyte on PTFE. The cell water balance problems at room temperature were only compounded by attempts to operate aqueous TFMSA cells at higher temperatures (60 to 70°C). Since the partial pressure of water increased significantly from ambient temperatures to 70°C, the aqueous TFMSA fuel cell was prone to electrolyte dryout. In some cases the acid concentration probably reached to nearly the monohydrate composition level previously shown to be very undesirable.

ENERGY RESEARCH CORPORATION

It became obvious shortly after initiation of this program that a trial and error approach to water balance would not be acceptable. The water balance factor became more complicated due to the lack of reliable vapor pressure data for TFMSA solutions. The available data showed inconsistencies between different investigators and generally was not at the concentrations of interest. Attempts were unsuccessful to correlate the available information into a meaningful estimation of water partial pressure as a function of acid concentration and temperature.

An analytical technique was finally utilized to predict the vapor pressures of various TFMSA solutions. The technique involves calculation of activity coefficients which essentially measure the deviations from ideal behavior of each component within the binary solution. The van Laar equations were utilized to determine the activity coefficients at various concentrations. Knowledge of the vapor pressure relationships of the two pure components (as well as the boiling point and composition of the azeotropic mixture) was utilized to derive the van Laar equations.

The van Laar equation is an empirical relationship which is thermodynamically consistent with the Gibbs-Duhem equation. It expresses a relationship between the activity coefficient ( $\gamma$ ) for a component in a binary solution as a function of only the mole fractions ( $X_1, X_2$ ) of each component within the solution. The van Laar equation can be written in the following form.

$$\log \gamma_1 = \frac{a}{\left(1 + \frac{X_1}{X_2} \frac{a}{b}\right)^2}$$

The two constants,  $a$  and  $b$  in the van Laar equation, can be determined if the activity coefficients for both components ( $\gamma_1, \gamma_2$ ) can be estimated at one particular concentration.

Raoult's Law states that the partial pressure of a component in an ideal solution is the product of the vapor pressure of the pure component times the mole fraction of that component in the liquid phase.

$$\bar{P} = P X$$

For a non-ideal solution such as TFMSA-water mixtures, the partial pressure deviates from Raoult's Law and is corrected by

**ENERGY RESEARCH CORPORATION**

a factor identified as the activity coefficient.

$$\bar{P} = \gamma P X$$

The partial pressure of a component, according to Dalton's Law, is also equal to the total pressure times the mole fraction of that component in the vapor phase.

$$\bar{P} = P_{\text{total}} Y$$

The activity coefficient can therefore be expressed as

$$\gamma = \frac{P_{\text{total}} Y}{P X}$$

The monohydrate of triflic acid is assumed to form a maximum boiling point azeotrope. The liquid and vapor phases for azeotropes have identical compositions, thus:

$$X = Y$$

A simple expression for the activity coefficient at the monohydrate composition is therefore:

$$\gamma = \frac{P_{\text{total}}}{P}$$

The total vapor pressure of the monohydrate is known to be 760 mm Hg at its boiling point (217°C).

The vapor pressure of pure water at 217°C is reported to be about 16420 mm Hg.<sup>11</sup> The vapor pressures of pure TFMFA have been reported at the following temperatures.

162°C	760 mm Hg
84°C	43 mm Hg
54°C	8 mm Hg

An extrapolated value for the vapor pressure of pure triflic

ENERGY RESEARCH CORPORATION

acid at 217°C could be determined from this data. As shown in Figure 1, this value was approximately 3600 mm Hg. An activity coefficient for both triflic acid and water could be calculated at the monohydrate composition where

$$(x_T = x_w = 0.5)$$

$$\gamma_T = 760/3600 = 0.2111$$

$$\gamma_w = 760/16400 = 0.0463$$

Since a van Laar equation for both TFMSA and water could be written at the monohydrate composition, the two constants within the equations could be determined.

$$a = -5.978$$
$$b = -3.027$$

The following equations were therefore derived for the activity coefficients of both components as a function of only the solution composition.

$$\log \gamma_T = \frac{-5.978}{\left(1 + \frac{x_T}{x_w} \frac{-5.978}{-3.027}\right)^2}$$

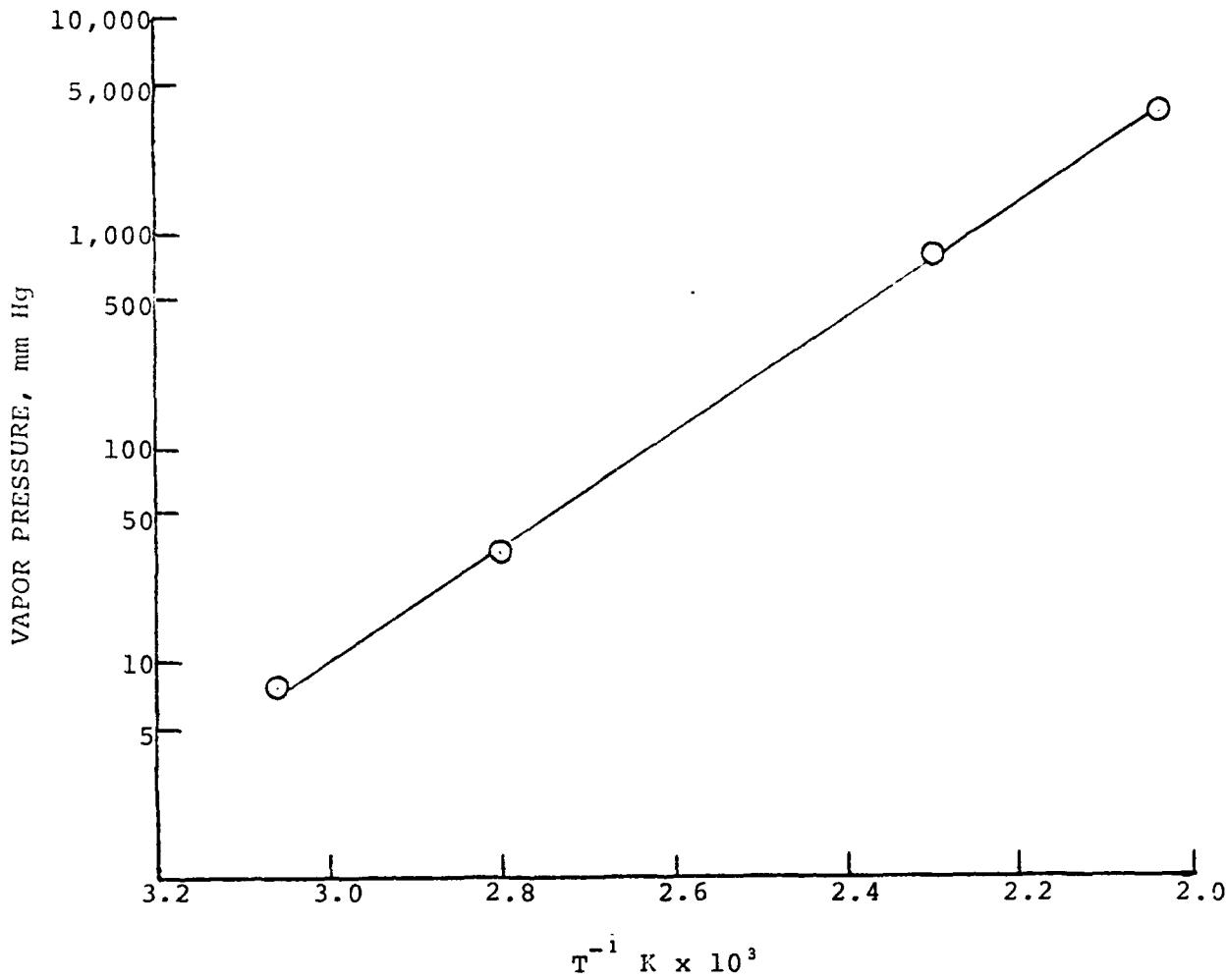
$$\log \gamma_w = \frac{-3.027}{\left(1 + \frac{x_w}{x_T} \frac{-3.027}{-5.978}\right)^2}$$

These equations were utilized to calculate the activity coefficients for TFMSA and water at various solution compositions. These values are summarized in Table 1 over the entire range of possible concentrations. A temperature of 60°C was arbitrarily selected as the elevated temperature of interest to be evaluated under this program. At this temperature:

$P_T$  = vapor pressure of pure TFMSA = 12 mm (Figure 1)

$P_w$  = vapor pressure of pure water = 150 mm

FIGURE 1  
VAPOR PRESSURES OF PURE TFMSA



D0988

TABLE I  
ACTIVITY COEFFICIENTS AND PARTIAL PRESSURES AT 60°C

$x_T$	$x_w$	$\gamma_T$	$\gamma_w$	Activity Coefficient		Partial Pressure, mm	Total Vapor Pressure, mm	Vapor Composition	
				$\bar{P}_T$	$\bar{P}_w$			$y_T$	$y_w$
0	1.000	.000001	1.000	0	1.50	150	150	0	1.000
.100	.900	.000095	.798	.00011	107.7	107.7	102.6	0	1.000
.109	.891	.000132	.768	.00017	102.6	102.6	102.6	0	1.000
.169	.831	.000905	.564	.0018	70.3	70.3	70.3	0	1.000
.200	.800	.0021	.467	.0050	56.0	56.0	56.0	0	1.000
.300	.700	.0176	.231	.063	24.25	24.25	24.31	.002	.998
.400	.600	.0769	.105	.369	9.45	9.45	9.82	.938	.962
.500	.500	.2111	.0463	1.27	3.47	3.47	4.74	.268	.732
.565	.435	.339	.0271	2.298	1.768	1.768	4.066	.565	.435
.600	.400	.416	.0203	3.00	1.218	1.218	4.22	.711	.289
.700	.300	.645	.0090	5.42	.405	.405	5.83	.930	.070
.800	.200	.840	.0041	8.06	.12	.12	8.18	.985	.015
.900	.100	.961	.0019	10.38	.03	.03	10.41	.997	.003
1.000	0	1.000	.00094	12	0	0	12	1.00	0

**ENERGY RESEARCH CORPORATION**

The partial pressures of each component at 60°C could therefore be calculated by the following relationships.

$$\bar{P}_T = \gamma_T P_T X_T$$

$$\bar{P}_W = \gamma_W P_W X_W$$

The total vapor pressure would be the sum of the individual partial pressures.

$$P_{\text{total}} = \bar{P}_T + \bar{P}_W$$

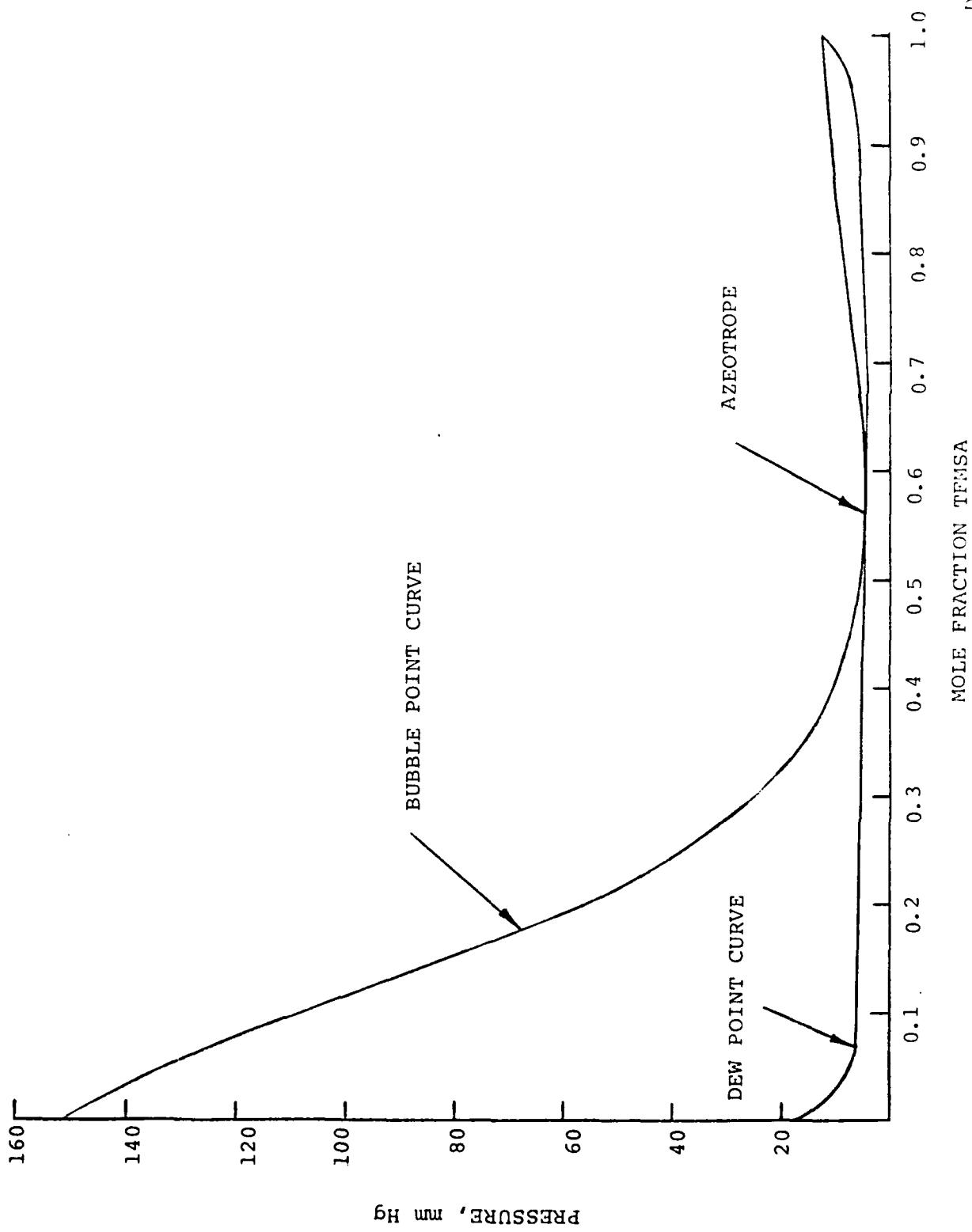
The vapor phase compositions could also be determined by:

$$Y_T = \frac{\bar{P}_T}{P_{\text{total}}} \quad Y_W = \frac{\bar{P}_W}{P_{\text{total}}}$$

The partial pressures, total vapor pressure, and vapor phase compositions for each solution are also reported in Table 1. It is significant to note from this data that when the mole fraction of TFMsa in the solution is 0.20 or less, the mole fraction of TFMsa in the vapor phase is insignificant compared to water. This would suggest that acid loss using dilute TFMsa solutions at 60°C will not be a severe problem. The low acid partial pressure values, however, cannot be totally ignored during long-term acid loss considerations. Also, by this analysis at 60°C, the apparent azeotropic composition is not exactly at 0.50 mole fraction but rather at 0.565 mole fraction TFMsa. This is the point at which: the total vapor pressure is at a minimum; and the liquid and vapor phases have identical values.

The data in Table 1 could be plotted to give a complete phase diagram of the TFMsa-water system at 60°C. As shown in Figure 2, the upper curve is a plot of the total vapor pressure as a function of the solution composition while the lower curve shows the total vapor pressure as a function of the vapor phase composition. The figure illustrates that the azeotropic composition is at 0.565 mole fraction and that the vapor pressures of dilute TFMsa solutions are essentially composed of 100% water.

FIGURE 2  
PHASE DIAGRAM OF TFMSA-WATER SYSTEM AT 60 °C



The van Laar technique is believed to be valid as an initial approximation of the vapor pressures of TFMSA solutions. The van Laar equations have been described as being reasonably consistent with experimental data for mixtures of organic liquids and water and in cases where the two constants (a and b) within the equations do not differ by more than a factor of two.<sup>5</sup> Although the van Laar constants probably are influenced to some degree by temperature, evaluation of such a dependency was outside the scope of this program.

Although reliable experimental vapor pressure data for aqueous TFMSA solutions was lacking at the initiation of this contract, some data did become available during the course of this study. American University obtained the vapor pressure data presented in Figure 3 utilizing an isopiestic technique.<sup>3</sup> The experimental data at 60°C, presented as a function of wt% TFMSA, was converted to mole fraction TFMSA. The experimental and analytical values for total vapor pressure are compared in Figure 4. A reasonable overall correlation did exist between the two methods, although differences were evident at some triflic acid concentration levels.

#### 2.1.2 Identification of Optimum Concentration

During Contract DAAK02-75-C-0045, four different TFMSA concentrations (25, 37.5, 50, and 60 vol%) were evaluated. These solutions correspond approximately to the 3, 4.5, 6, and 7.1 molar concentrations, respectively. In general, the more dilute electrolytes appeared to give the highest fuel cell performance levels; however the most stable cells contained the 50 and 60 vol% acid. The most important properties of TFMSA solutions relating to actual fuel cell use are believed to be:

- ionic conductivity
- wettability with PTFE
- acid partial pressure
- water partial pressure

All of the above characteristics are very concentration-dependent. The ideal triflic acid solution would possess a maximum ionic conductivity, a minimum acid partial pressure, and have no wetting tendency with PTFE. This might suggest that the very dilute solutions would be preferable. However at low acid concentrations, the high water partial pressures would make fuel cell water management difficult. A trade off between the optimum electrolyte characteristics would probably be necessary.

Recently American University completed an extensive study of the properties of TFMSA relating to fuel cell use.<sup>9</sup> This

FIGURE 3  
EXPERIMENTALLY OBTAINED VAPOR PRESSURES OF TFMSA SOLUTIONS

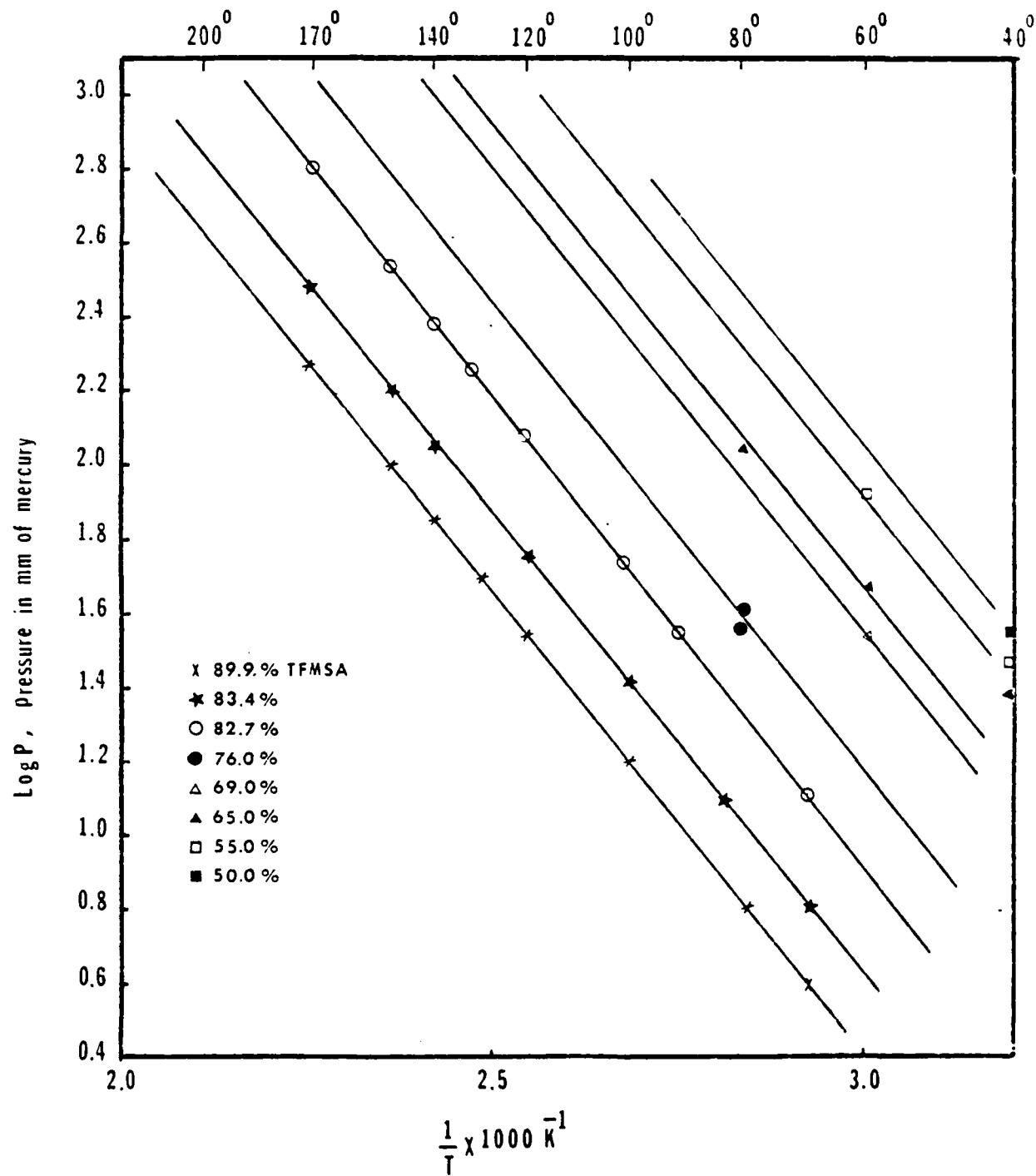
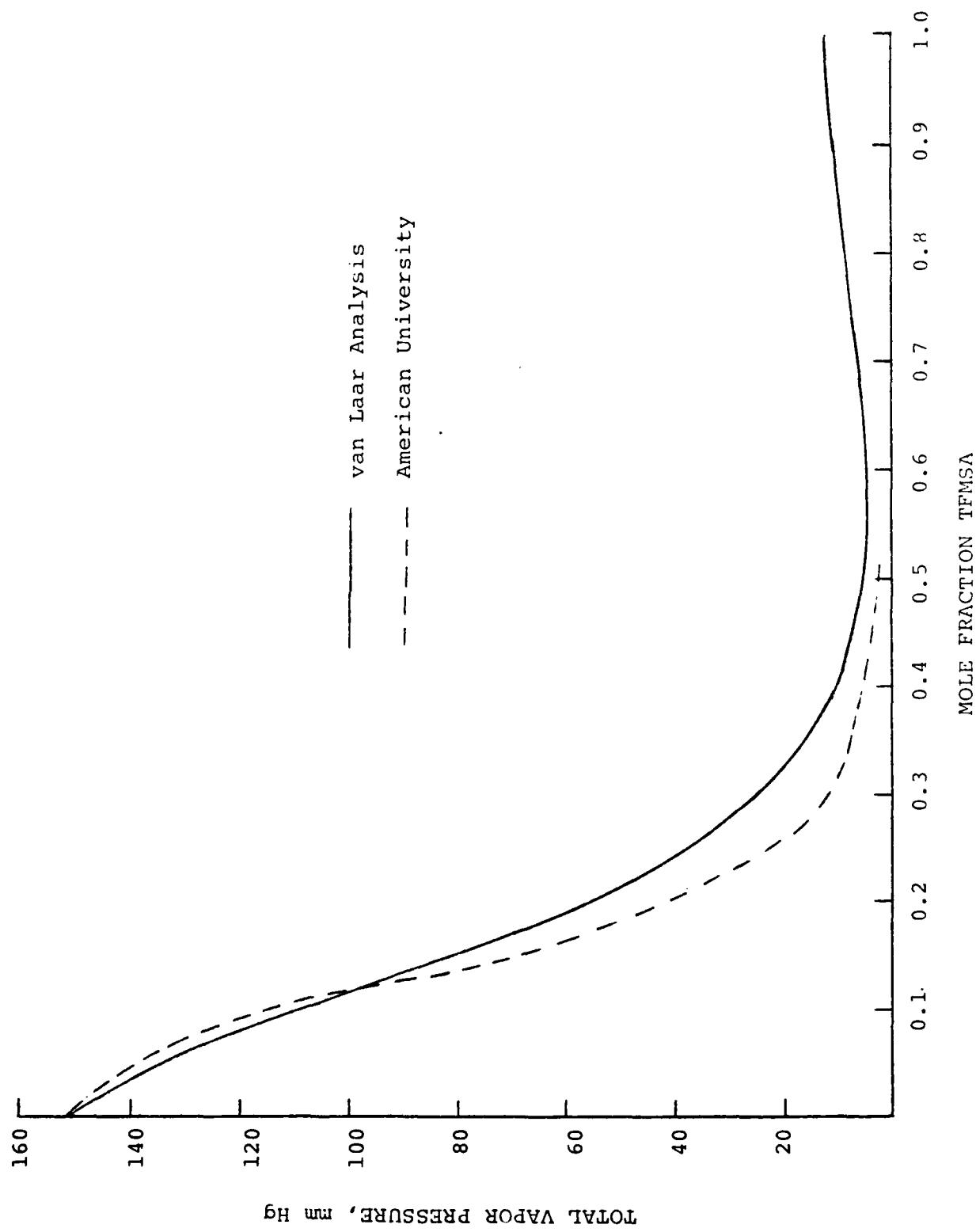


FIGURE 4

VAPOR PRESSURES OF TFMSA-WATER SOLUTIONS AT 60°C



proved useful in selecting triflic acid concentrations to be evaluated under this program. In Figure 5, ionic conductivities of various TFMSA solutions are shown as a function of temperature and concentration. Since the American University data at 40°C gave the same profile as the ERC data at 25°C, conductivity values were also estimated at higher temperatures. Estimation of the profile at 80°C was aided by the fact that the maximum conductivity has been reported to be  $0.81 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

American University also conducted a study to quantitatively determine the wetting tendencies of TFMSA solutions with PTFE. The extent of wetting is measured by the contact angle between the liquid and solid: a contact angle of 90° is considered to be nonwetting while 0° indicates total wetting. In Figure 6, the contact angles of various TFMSA solutions with PTFE are shown as a function of electrolyte concentration. The tendency for a fuel cell electrode to flood is generally enhanced with the more concentrated TFMSA solutions. This observation correlates well with the contact angle measurements.

Partial vapor pressures for both acid and water could be calculated utilizing the activity coefficients determined by the van Laar method. The acid partial pressure would be important as it relates to the amount of acid loss experienced by a cell during continual operation. Acid loss would increase as the acid concentration increases. Table 2 summarizes the partial pressures of each component as well as the ionic conductivities and contact angles for each of the TFMSA solutions under consideration. The properties are presented at 60°C, an operational goal selected for this program. Undoubtedly the optimum electrolyte concentration will be influenced to some degree by cell temperature. Concentration of the acid would naturally occur as the cell temperature is increased. A temperature of 60°C was selected because some investigators have indicated that acid decomposition begins to occur at this point.<sup>6</sup>

The stoichiometric air flow rate necessary to maintain a constant acid concentration within an operating fuel cell is presented in Table 2 for each of the proposed TFMSA solutions. These values were calculated by making an appropriate material balance of the cell products and reactants during operation. It was assumed that a constant acid concentration would be maintained if all water produced within the cell was removed by the air stream through the cell. This would require that the average of the water partial pressures within the inlet and outlet air streams equal the water partial pressure of the original electrolyte. Since the inlet water partial pressure is generally known ( $\approx 20 \text{ mm Hg}$  for saturated air at ambient temperature), the outlet water partial pressure can be determined. Thus at the cell outlet, the following relationship is valid.

FIGURE 5

CONDUCTIVITIES OF TFMSA-WATER SOLUTIONS

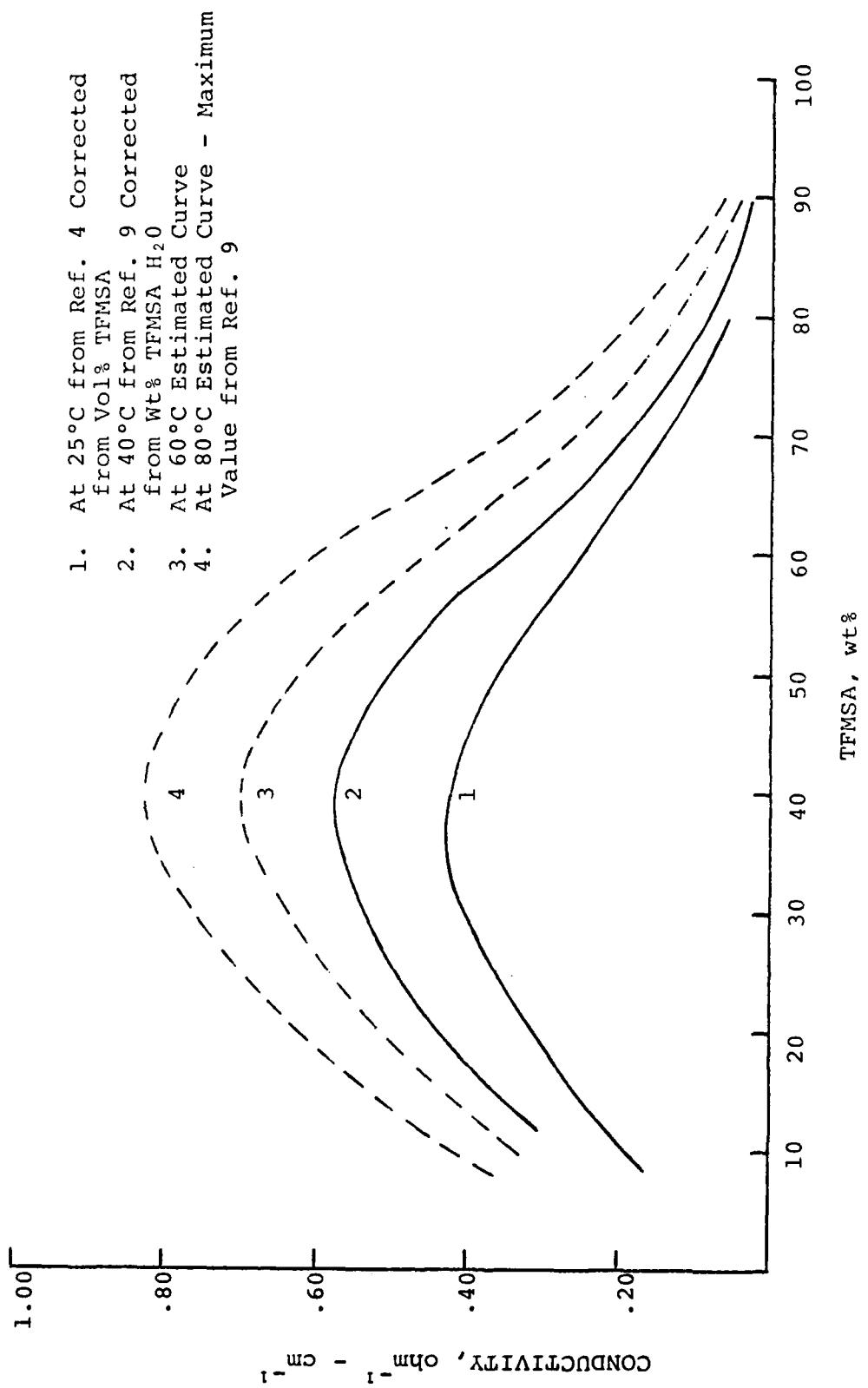
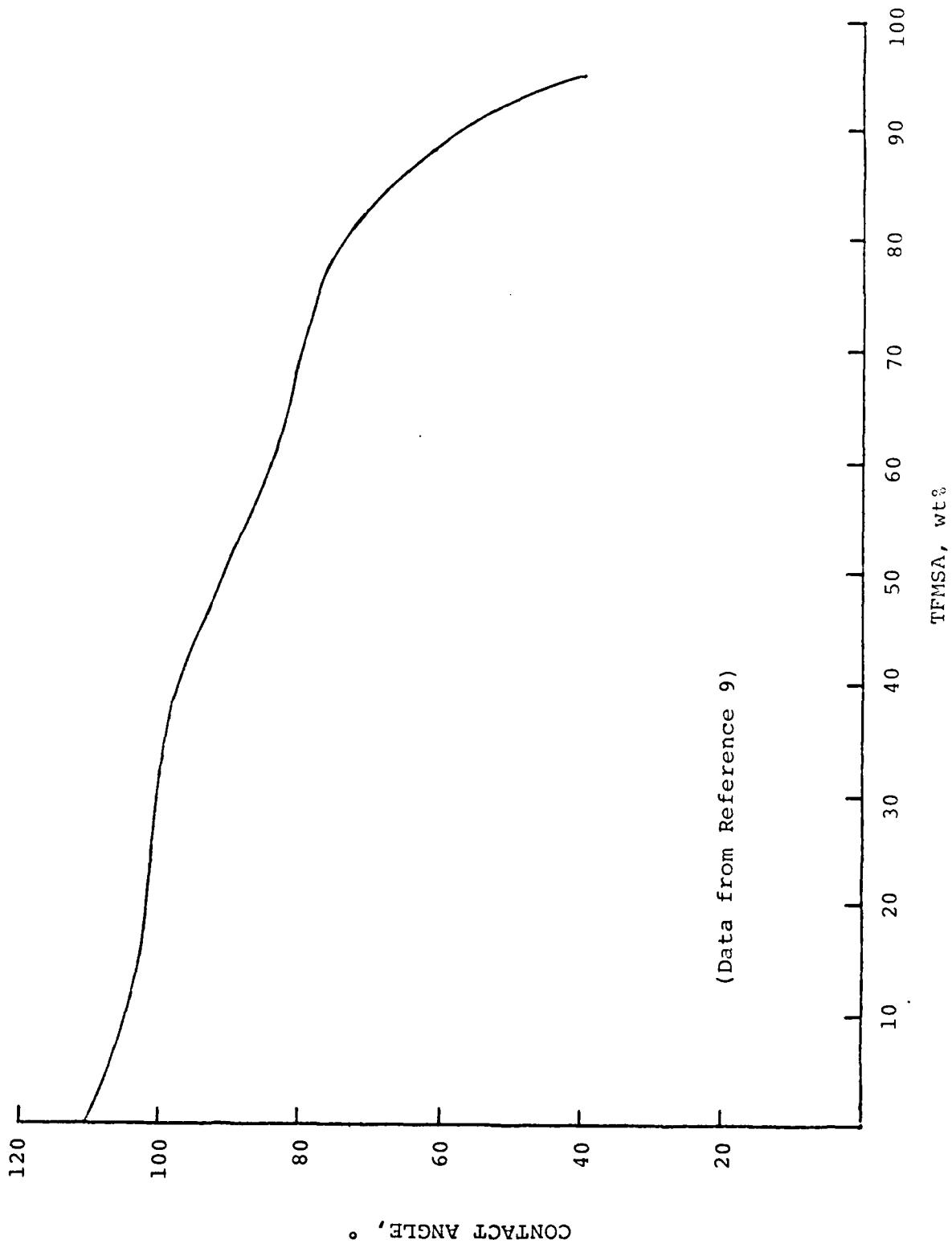


FIGURE 6  
CONTACT ANGLES OF TFMSA-WATER SOLUTIONS ON PTFE



## ENERGY RESEARCH CORPORATION

TABLE 2  
PROPERTIES OF TFMSA-WATER SOLUTIONS AT 60°C

Properties	Molar Concentrations			
	3	4.5	6	7.1
Solution, vol%	25	37.5	50	60
TFMSA, wt%	36.1	50.4	62.9	71.8
TFMSA, Mole Fraction	.063	.109	.169	.234
Conductivity ( $\text{ohm}^{-1} - \text{cm}^{-1}$ )	.70	.63	.40	.23
Contact Angle on PTFE, °	98	91	83	78
Partial Pressure TFMSA, mm Hg	.000016	.00017	.0018	.0132
Partial Pressure Water, mm Hg	127	102.6	70.3	42.8
Stoichiometric Air Flow Rate Required	1.2	1.5	2.5	4.6

$$\frac{\bar{P}_{H_2O}}{760 - \bar{P}_{H_2O}} = \frac{\text{moles } H_2O \text{ (enter)} + \text{moles } H_2O \text{ (produced)}}{\text{moles air (enter)} - \text{moles } O_2 \text{ (consumed)}}$$

The required air flow rate could therefore be calculated.

As shown in Table 2, the 3 M and 4.5 M triflic acid solutions did offer some attractive advantages: high conductivities, high contact angles with PTFE, and low acid partial pressures. The low air flow rates required to maintain water balance, however, would tend to make fuel cell operation problematic. The fuel cell would become air starved and severe polarization losses would occur due to low average oxygen partial pressures. The 6 M TFMSA electrolyte, therefore, appears to be the approximate optimum concentration for use at 60°C. (The dilute concentrations would be attractive at lower temperatures.)

## 2.2 Experimental Procedures

### 2.2.1 Electrode Fabrication

The fuel cell electrodes prepared for this program consist of a catalyst layer mounted on an electrode substrate. Fabrication techniques have generally been identical to those previously developed for phosphoric acid fuel cell electrodes. The catalyst layer, consisting of the electrocatalyst and a binder, could be prepared utilizing two completely different techniques. One method involves use of a machine calendering mill in which a thin, discrete catalyst layer with excellent structural integrity is formed by essentially a rolling operation. The second method, described as a sheet mold process, involves depositing the electrocatalyst-binder mixture directly on the electrode substrate. Differences in performance of electrodes prepared by the two techniques have previously been shown to be insignificant when tested in phosphoric acid fuel cells. During this program, the method of preparation did have some bearing on the subsequent electrode performance.

The rolling process initially consists of wet blending the electrocatalyst with a dry PTFE powder and a filler in a petroleum distillate type of medium. The filler, a decomposable material (ammonium bicarbonate), serves to aid in ease of handling during the rolling operation. After allowing the solvent to evaporate over a period of several days, the filler is removed by gentle heating. The resulting catalyst layer is bonded to the electrode substrate at a pressure of 300 psi. The electrode substrate is a highly porous and

conductive carbon fiber paper, as produced by the Stackpole Carbon Company. The substrate is also wetproofed with FEP (a copolymer of tetrafluoroethylene and hexafluoropropylene) to prevent electrolyte entrapment within its pores. The FEP content of the electrode backing is generally in the range of 35 to 40%.

Electrodes produced by either the rolling or sheet mold process are then subsequently sintered at 350°C for a period of 20 minutes. The sintering operation gives a hydrophobic nature to the catalyst layer to prevent flooding and to insure ready gaseous reactant access to the electrocatalyst.

Three different electrocatalysts were selected for evaluation during this study: Pt black, Pt on carbon black, and Pt on Kocite. Emphasis was initially placed on Pt black type electrodes since the supported catalyst type had previously proven to be difficult to operate. These difficulties were attributed to an inability to effectively wet the electrocatalyst with the TFMSA electrolyte. All Pt black electrodes were prepared by the rolling process and contained 2 to 4 mg/cm<sup>2</sup> of Pt. Most Pt black electrodes contained 25 wt% PTFE. Later in the program, Pt on Kocite electrodes were effectively utilized. These electrodes generally contained 0.50 to 0.60 mg/cm<sup>2</sup> Pt and 45 wt% PTFE. Although acceptable performance levels could not be obtained for rolled Pt on carbon black electrodes, similar electrodes prepared by the sheet mold process did give promising results. A PTFE content of 40 wt% appeared to be an optimum for use with the carbon black electrodes.

### 2.2.2 Fuel Cell Assembly and Testing

A systematic determination of the kinetic parameters affecting TFMSA fuel cells was not conducted during this program. Therefore no attempt was made to evaluate electrodes in half cell test apparatus. All efforts were directed at developing a practical triflic acid fuel cell using real fuel cell components at conditions which simulate a real fuel cell environment. All testing was performed within model subscale size full cells utilizing pure hydrogen as the fuel and either air or oxygen as the oxidant. Test electrode size was standardized at 25 cm<sup>2</sup> throughout the program.

Cell assembly techniques and test procedures were similar to those currently utilized for phosphoric acid fuel cells. Cell components (such as matrices and test plates) were also identical to those optimized for use with phosphoric acid with one major exception. At the low temperatures of interest under

ENERGY RESEARCH CORPORATION

this program, a glass fiber matrix could be effectively utilized.

All cells were constructed within molded graphite hardware. The graphite plates were a composite structure of a commercially available graphite and a phenolic type resin. The anode plate also contained a reservoir for periodic electrolyte addition. The reservoir was in intimate contact with the cell matrix which extended beyond the periphery of the cell electrodes. During previous aqueous TFMSA programs, some difficulties were experienced in adequately sealing the reservoir area, as the electrolyte tended to readily leak from the cell. An O-ring sealing technique was successfully employed to overcome this problem. During this program, improved dimensional control of the test plates allowed elimination of the O-ring technique. Adequate sealing was provided through use of PTFE gaskets.

Glass fiber and silicon carbide were extensively utilized as cell matrix materials during this study. The glass fiber matrix is a commercially available filter paper (Reeve Angel 934AH). Although its bubble pressure is relatively low, gas reactant crossover was generally not a major problem and thus consistent cell builds could be made. The glass fiber paper was highly porous and was readily compressed during cell assembly. The silicon carbide matrix was a composite structure consisting of a particulate SiC and PTFE binder. The matrix is formed directly on the electrode structure utilizing a bar casting technique. The porosity of the resulting SiC matrix is only about 50% and thus is not readily compressed during cell assembly.

The cell assembly procedure consisted of initially saturating the cell matrix with electrolyte and compressing it between the two dry electrode structures. Partial filling of the electrodes occurred during the assembly process and further wetting also occurred during cell operation. Some electrodes proved to be difficult to wet. At times, electrode wetting could be enhanced by electrode pre-polarization and cell reversal procedures. Operation at 60°C also appeared to aid the wetting characteristics of the electrocatalysts contained within the electrode structures. All cells constructed during this program have contained identical electrodes, tested as both anode and cathode. As in the case of most acid fuel cells, cell performance was normally cathode limited. An abnormally dry anode could at times influence overall cell performance. This generally occurred shortly after cell assembly and could be alleviated by switching the reactant gas flows to the individual electrodes.

FC-24 produced by the 3 M Company was utilized exclusively as the triflic acid evaluated for fuel cell use. No attempt

was made to purify the as-received acid; it was simply added to water to produce the desired final concentration. Considerable heat was evolved during the mixing process and a volume loss of about 5% was generally observed. Periodically the resulting solution had a slight yellowish tint but it could not be determined whether this discoloration had any detrimental effect on subsequent fuel cell performance.

Actual fuel cell testing normally consisted of passing pure hydrogen to the anode and air to the cathode. Performance data on oxygen was also obtained to serve as a diagnostic aid. The difference between air and oxygen performance ( $O_2$  gain) is a measure of the diffusional losses existing within a fuel cell electrode. The air flow rate to operating cells was generally controlled to maintain a constant acid concentration. It has become apparent during this program that the entering air must be humidified to prevent electrolyte dryout at the cell inlet. The hydrogen flow was held at a minimum purge rate to eliminate the possibility of significant water rejection occurring at the anode.

### 2.3 Results and Discussion

The major objective of this program has been to demonstrate that aqueous TFMSA fuel cells can be operated stably for long periods both at ambient and elevated temperatures. The demonstration of high cell performance with low loaded supported catalyst type electrodes was also given priority. The specific goals have included a minimum hydrogen-air performance level of 650 mV at 100 mA/cm<sup>2</sup> and a cell endurance capability of at least 2500 hours. Generally the minimum performance goal posed no major difficulties even during the initial contract stages. Many cells, especially those with high loaded Pt black electrodes, easily surpassed the contract requirements. However the endurance goal presented a more formidable challenge.

Approximately 100 subscale TFMSA fuel cells were assembled and tested. Initial emphasis was placed on obtaining maximum performance levels. Although many of the initial cells exhibited high potentials, a few cells had extremely low load carrying capabilities. This was prevalent in cells containing Pt black electrodes with 30% or greater PTFE content and Pt on carbon black electrodes with more than 45% PTFE content. These cells were marked by the presence of low open circuit voltages which implied that little electrolyte had penetrated into the electrode structures. Attempts to wet the high PTFE content electrodes by various high and low cathode prepolarization treatments generally were unsuccessful.

The most reproducible test results were obtained with Pt black electrodes containing 25% PTFE. Acceptable performance levels generally could be attained within 24 hours after initial startup even at ambient temperature. A typical performance curve for 2 mg/cm<sup>2</sup> loaded Pt black electrodes with 6M TFMSA as the electrolyte at room temperature is shown in Figure 7. Although the performance was acceptable by acid fuel cell standards, the cells generally showed very erratic behavior. Cell instability was accentuated when attempts were made to continually operate cells at current densities as high as 200 mA/cm<sup>2</sup>. Also evident was the fact that for many cells, the oxygen gain increased significantly as a function of current density. This suggested that electrode flooding was prevalent. When flooding became apparent, the cells were air sensitive and at times could be unflooded by merely increasing the air flow rate. The air flow was generally maintained at about the 7 to 10 stoichiometric rate (or 7 to 10 stoich) although periodically it was adjusted in an attempt to stabilize cell performance. It became obvious after operating a number of similar type cells that the water production within the cell was creating significant electrolyte changes; these, in turn, probably caused the apparent electrode flooding tendency.

A large batch of identical Pt black type electrodes was prepared in order to conduct a systematic evaluation of the water balance problems within TFMSA cells. Since Pt black electrodes are no longer utilized in phosphoric acid fuel cells at ERC, the electrodes were inadvertently prepared with twice the normal Pt loading. However these electrodes did result in consistent initial performance levels in aqueous TFMSA fuel cells. Two of every three TFMSA cells assembled gave cell terminal voltages estimated to be at least 50 mV higher than for similarly loaded electrodes operating with  $\approx$ 100% H<sub>3</sub>PO<sub>4</sub> at 180°C. These 4 mg/cm<sup>2</sup> loaded Pt black electrodes were also selected for evaluation at elevated temperature. As shown in Figure 8, a cell terminal voltage of 760 mV at 200 mA/cm<sup>2</sup> was obtained on pure hydrogen and air at 60°C. A typical internal resistance for these cells was .006Ω which resulted in an IR loss of only 15 mV per 100 mA/cm<sup>2</sup>. At 200 mA/cm<sup>2</sup> the cathode potential was therefore at least 790 mV. The internal resistance of the triflic acid cells at 60°C was generally lower than that experienced with phosphoric acid cells. A typical value of .010 to .012Ω is normally obtained for cells with  $\approx$ 100% H<sub>3</sub>PO<sub>4</sub> at 180°C. The lower resistance of the triflic acid cells (compared to phosphoric acid cells) was probably due to the thin and porous nature of the glass fiber matrix utilized rather than to any improved electrolyte conductivity.

In Figure 9, the IR free data for the 4 mg/cm<sup>2</sup> Pt black

FIGURE 7

PERFORMANCE OF Pt BLACK ELECTRODES  
with 2 mg/cm<sup>2</sup> Pt Loading

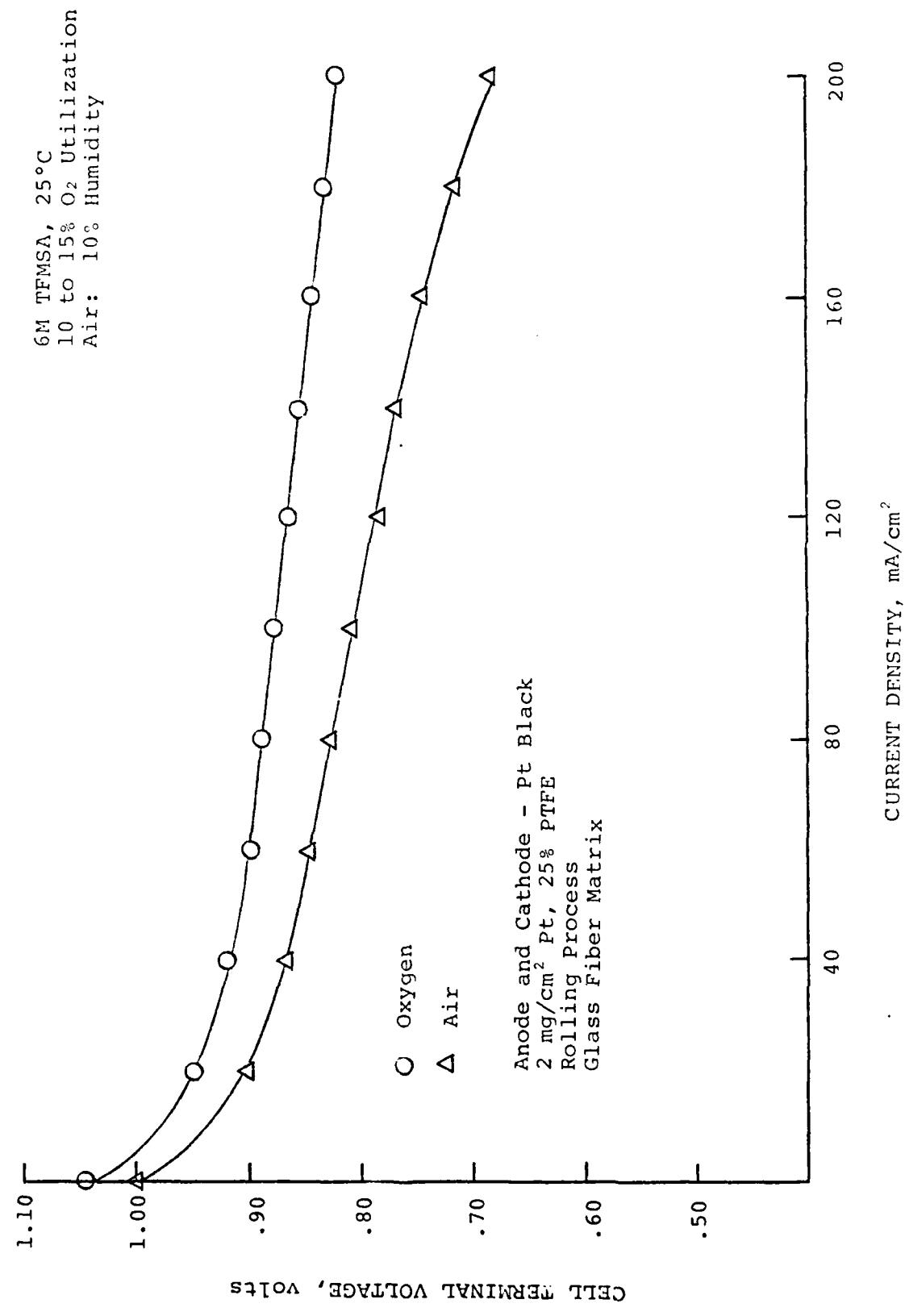


FIGURE 8

PERFORMANCE OF Pt BLACK ELECTRODES  
with  $4 \text{ mg/cm}^2$  Pt Loading

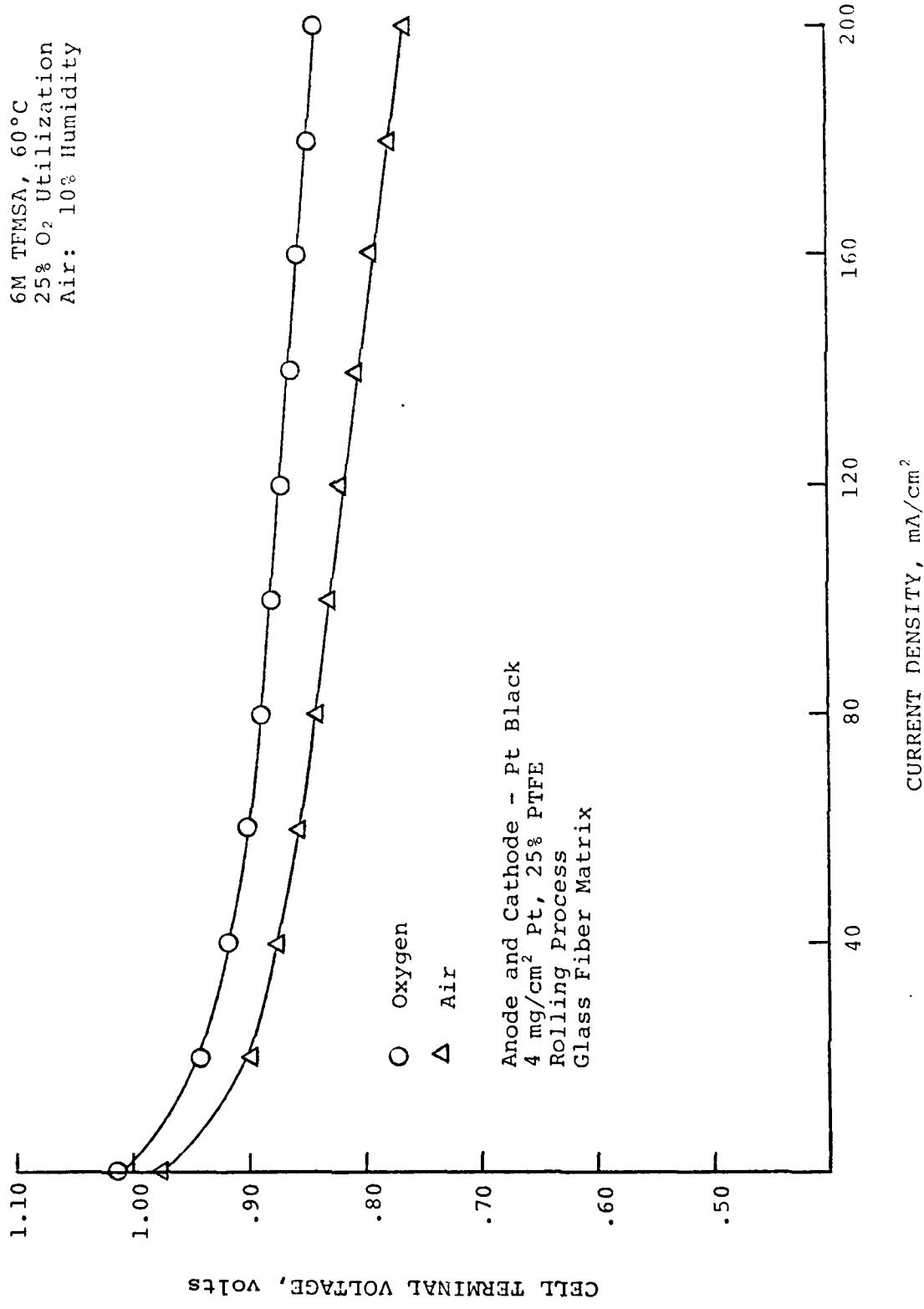
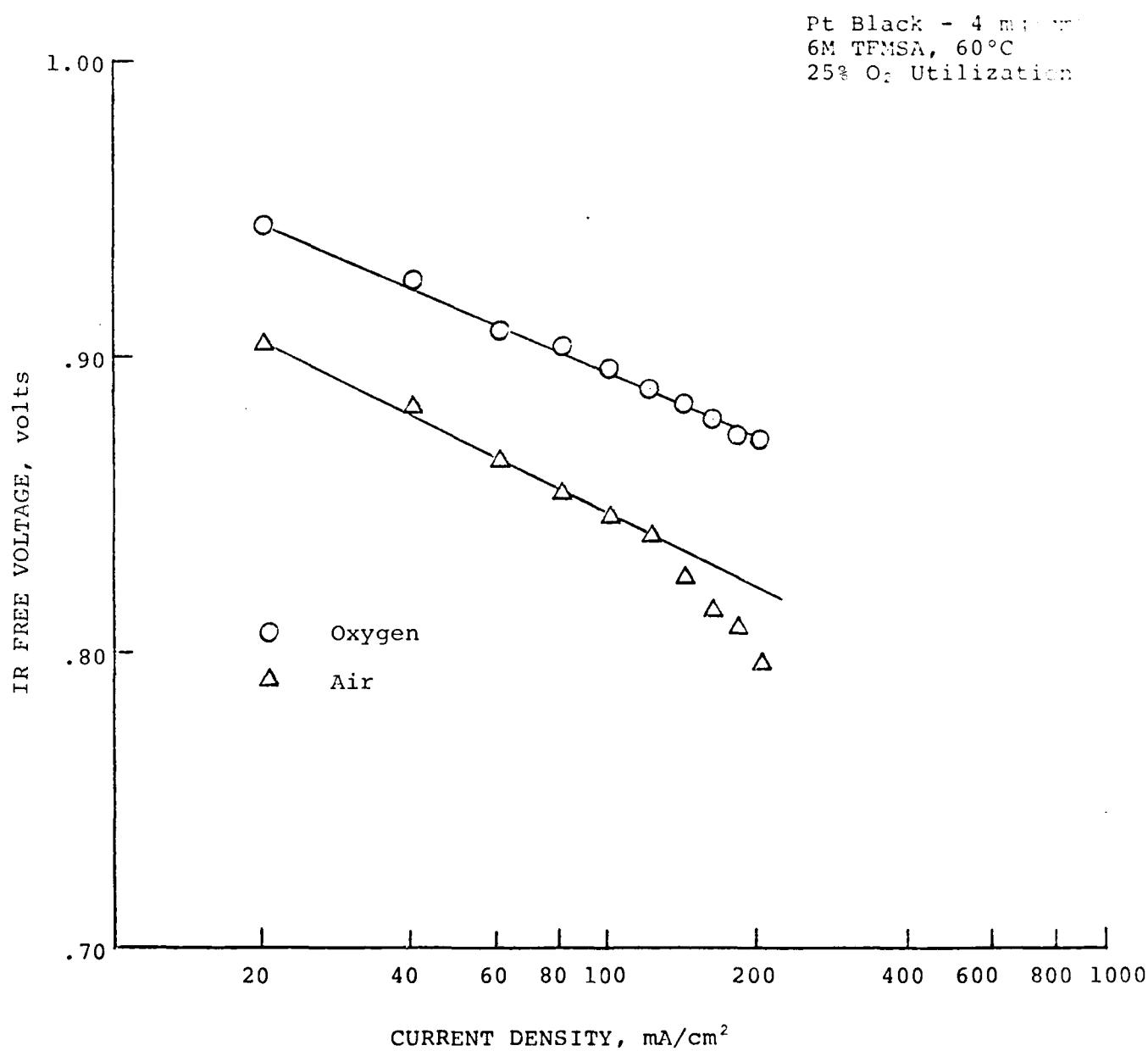


FIGURE 9  
TAFEL PLOT OF 4 mg/cm<sup>2</sup> Pt BLACK ELECTRODE



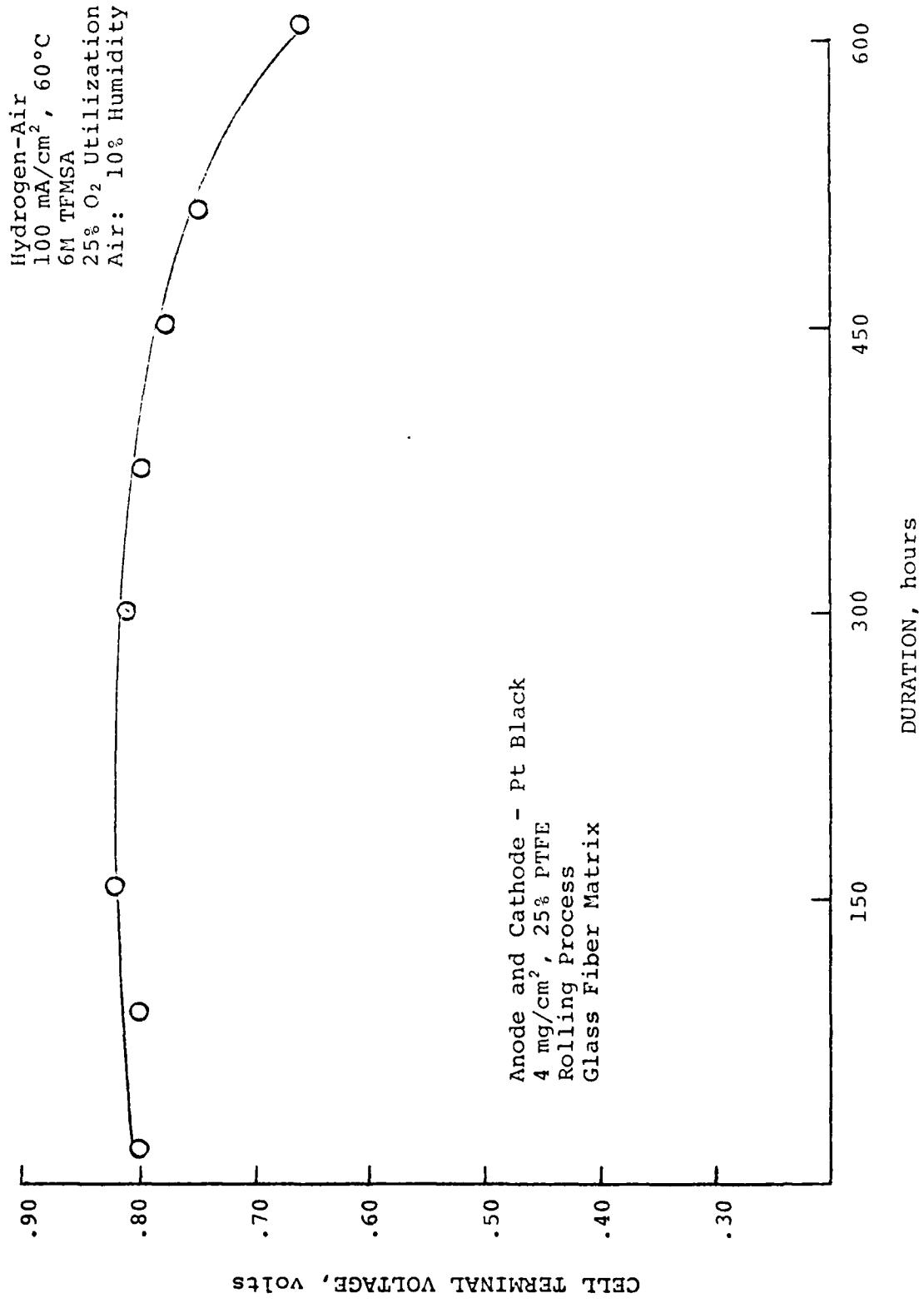
ENERGY RESEARCH CORPORATION

electrodes is plotted on semilog graph paper. As shown, the Tafel slope for the oxygen performance data was approximately 70 mV per decade. This experimentally obtained Tafel slope approximates the 66 mV per decade value predicted by theory if the Tafel slope is equivalent to  $2.303 \text{ RT/F}$ . A 70 mV Tafel slope on oxygen was not obtained for every cell. A slope between 80 and 90 mV per decade appeared to be more typical. In some cases, two distinct slopes were observable. This generally occurred when severe electrode flooding due to inadequate cell water balance was suspected.

The data presented in Figures 8 and 9 is considered to be equilibrium cell performance in which the potentials were maintained at least for a period of 24 hours. In many cases, the performance could be temporarily increased by prepolarizing the cell cathode. This treatment has been described previously in conjunction with phosphoric acid cathodes.<sup>7</sup> Performance gains by prepolarization were significantly greater in TFMSA cells than are normally obtained with phosphoric acid fuel cells. At times it was possible to momentarily increase TFMSA cell performance by 50 to 70 mV following a cathode prepolarization treatment. TFMSA cells with  $4 \text{ mg/cm}^2$  loaded Pt black electrodes were actually observed to operate in excess of 800 mV (cell terminal at  $200 \text{ mA/cm}^2$  on hydrogen and air) for short durations. The cathode prepolarization treatment was simply performed by shutdown of the air supply to an operating cell under load. This would exhaust the oxygen within the cell and drive the cathode potential toward the anode potential.

Initial endurance testing of triflic acid fuel cells at  $60^\circ\text{C}$  did involve a trial and error approach to the water balance problem existing within continually operating cells. Water balance control was emphasized at the elevated temperature rather than at ambient temperature. It was rationalized that  $60^\circ\text{C}$  would more closely simulate actual operating conditions existing within any projected TFMSA fuel cell system. Any practical system involving multi-cell units would produce significant heat, automatically setting higher cell operating temperatures. The trial and error approach involved maintaining various air flow rates to continually operating cells. One cell at  $60^\circ\text{C}$  did show reasonable stability for a period of several weeks with an air flow equivalent to about 4 stoich. As shown in Figure 10, eventual cell decay occurred which appeared to be mainly related to electrode flooding. The flooding was evident by the large increase in oxygen gains with time. It was not then clear whether the flooding tendency was created by electrolyte dilution or electrolyte concentration. During operation, electrolyte was replenished to the cell on a regular basis since acid loss was suspected to be a major problem at  $60^\circ\text{C}$ .

FIGURE 10  
ENDURANCE OF Pt BLACK ELECTRODES



ENERGY RESEARCH CORPORATION

It became obvious after operating numerous, unstable 6M TFMSA cells at 60°C that additional data pertaining to the partial pressures of TFMSA-water solutions would be required to make significant advances in TFMSA fuel cell technology. At this time, the van Laar analysis, as presented previously, was conducted. The initial van Laar calculations predicted that the partial pressures for water and TFMSA would be 67 mm Hg and .0014 mm Hg, respectively, for the 6M TFMSA solution at 60°C. This value for the partial pressure of water allowed calculation of an air flow rate to operating cells which would maintain the average acid concentration within the cell at 6M. If the entering air was at ambient temperature and had a relative humidity of 10%, a flow equivalent to 2.2 stoich would be necessary. If the inlet ambient temperature air was saturated, the air flow could be increased to about 3 stoich. Attempts to operate cells for extended periods with the dry inlet air were unsuccessful. As shown in Figure 11, significant cell decay occurred after 300 hours of operation presumably due to electrode flooding. Later it was concluded that the dry air would have a tendency to remove water from the electrolyte near the inlet air portion of the cell. This localized concentration of the acid would have an adverse effect on the wetting of PTFE by the electrolyte.

Use of humidified entering air appeared to improve the subsequent stability of 6M TFMSA cells operating at 60°C. A 2100 hour endurance plot for Pt black electrodes is presented in Figure 12. As shown, reasonable stability was maintained for a period of 1600 hours when operating continually at 200 mA/cm<sup>2</sup> on hydrogen and air. After that time, significant decay was evident due to both crossover and electrode flooding. The electrode flooding was probably caused by loss of water balance within the cell. The loss of water balance may have been due to improper control of cell operational parameters.

A slight modification was made within the original van Laar analysis during the course of this study. An extrapolated value of 19000 mm Hg had been utilized initially for the vapor pressure of water at 217°C. This was corrected to 16420 mm Hg when a literature value was found. Recalculation of the partial pressures at 60°C indicated that values of 70.3 mm Hg and .0018 mm Hg would be more accurate for water and TFMSA, respectively. This modification essentially lowered the predicted optimum air flow from about 3 to 2.5 stoich. Since the van Laar analysis is probably not absolutely precise, changes were not performed in the air flow rates of existing cells on endurance test.

After improvements were made regarding the water management problem, subsequent emphasis was placed on the evaluation

FIGURE 11

ENDURANCE OF Pt BLACK ELECTRODES  
with Dry Air

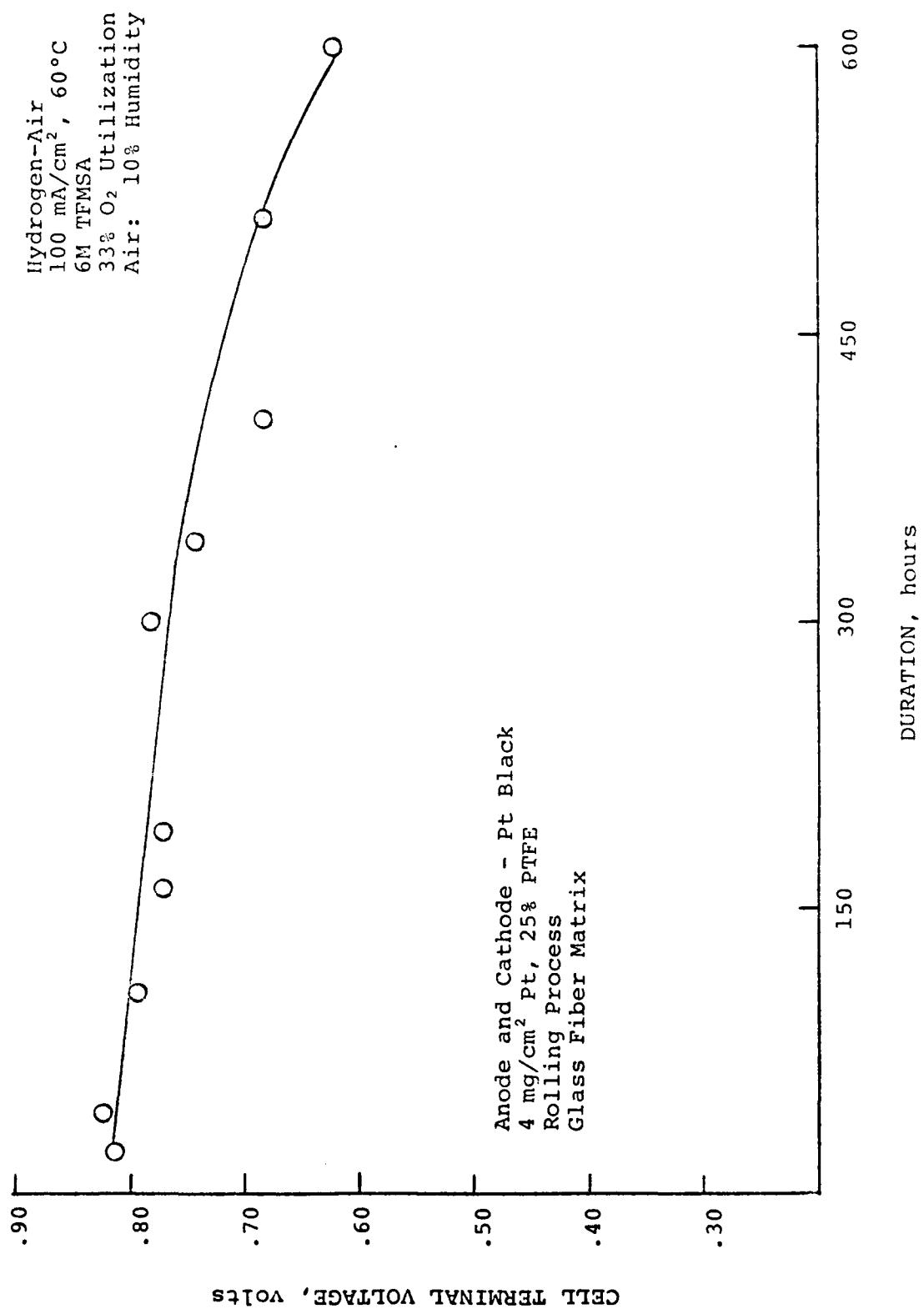
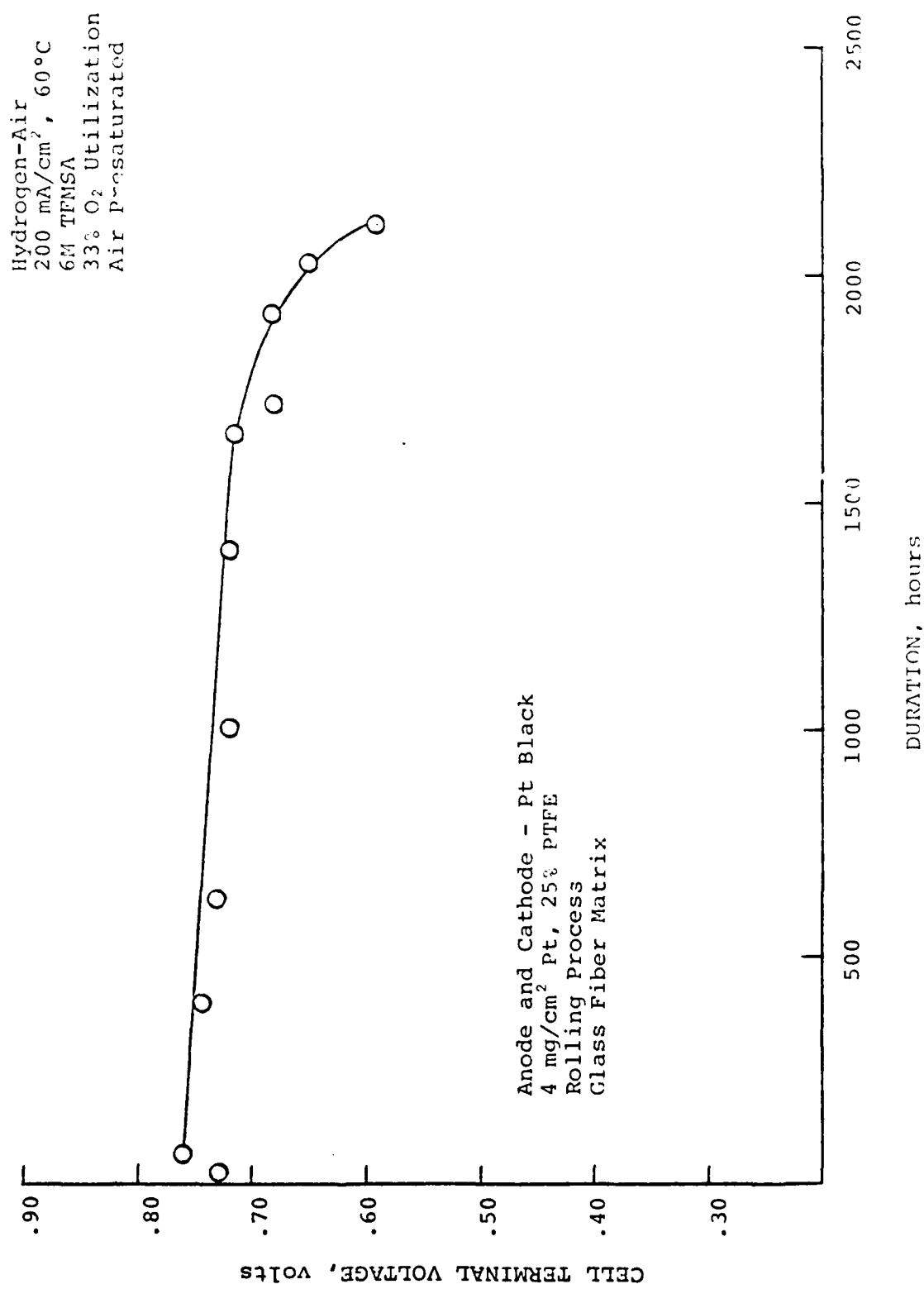


FIGURE 12

ENDURANCE OF Pt BLACK ELECTRODES  
with Presaturated Air



of supported catalyst type electrodes in triflic acid fuel cells. The Pt on carbon black type electrodes currently utilized in phosphoric acid fuel cells continued to pose difficulties in TFMSA fuel cells. Very inconsistent test results were generally obtained with the Pt on carbon black catalyst especially during the first half of this contract. Since alternate supported catalysts (such as Pt on Kocite) were made available for this program, a significant influence of catalyst on cell performance was observed. Pt on Kocite is a proprietary electrocatalyst of UOP Inc. and its optimization for use in phosphoric acid fuel cells was performed during Contract No. DAAG53-76-C-0014, a joint UOP-ERC effort. One batch of Pt on Kocite, designated 3648-115, gave reasonably reproducible performance levels in TFMSA fuel cells. This batch was prepared utilizing a platinum diammino dinitrite impregnation technique in conjunction with a Kocite material derived from Hydral alumina. A polarization curve for an electrode structure prepared from 3648-115 Kocite electrocatalyst by the rolling process and containing .64 mg/cm<sup>2</sup> Pt and 45 wt% PTFE is presented in Figure 13. This identical electrode had been evaluated with phosphoric acid electrolytes during Contract No. DAAG53-76-C-0014.<sup>12</sup> In Figure 14, a comparison is made between the hydrogen-air performance of the same electrode in 6M TFMSA and 101.6% H<sub>3</sub>PO<sub>4</sub>. The cells differed only with respect to operating temperature and the cell matrix. (A Kynol matrix was utilized within the phosphoric acid cell.) As shown, the air performance of the triflic acid cell at 200 mA/cm<sup>2</sup> was 50 mV higher than for the phosphoric acid cell. Twenty mV of this difference was attributed to a lower cell resistance. The lower cell resistance was probably due to the thin nature of the glass fiber matrix utilized in the triflic acid cell. In Figure 15, a 2300 hour endurance history of Pt on Kocite electrodes with 6M TFMSA electrolyte is presented. Reasonable cell stability was maintained for a period in excess of 2000 hours. Eventual cell failure appeared to be related to electrode flooding.

Pt on carbon black catalysts were successfully employed in TFMSA fuel cells when the sheet mold electrode fabrication technique was substituted in place of the calendering process. As shown in Figure 16, performance levels equivalent to similarly loaded Pt on Kocite electrodes could be obtained. The reason for the improved results with the sheet molded electrodes over the rolled electrodes with the Pt on carbon black catalyst is not precisely known: It probably was due to improved Pt utilization within the sheet molded electrode structure. A cell with the Pt on carbon black type electrodes was successfully operated for approximately 3900 hours. The endurance plot (Figure 17) indicates that acceptable stability

FIGURE 13

## PERFORMANCE OF Pt ON KOCITE ELECTRODES

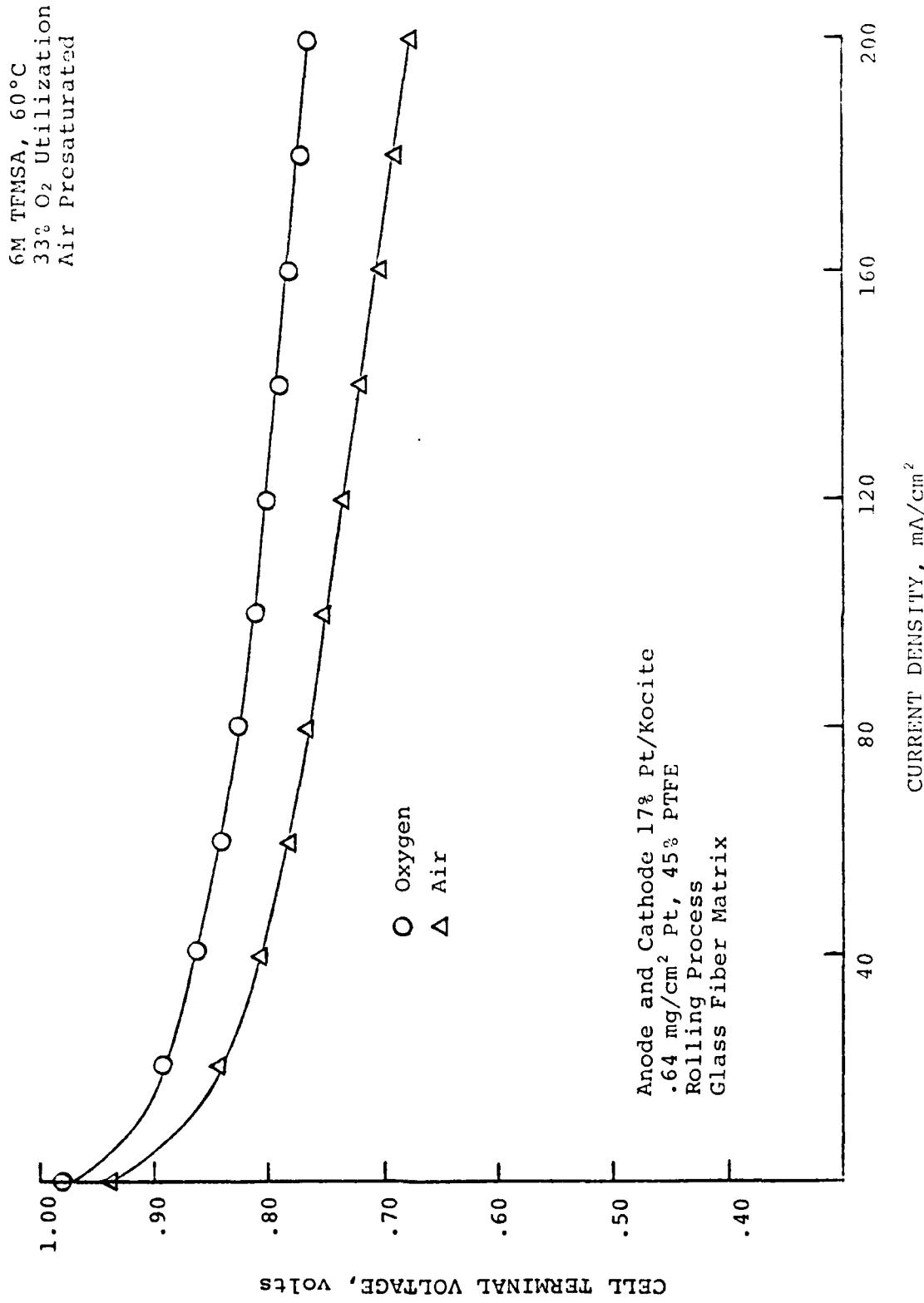


FIGURE 14

COMPARISON OF ELECTRODE PERFORMANCE IN TFMSA AND H<sub>3</sub>PO<sub>4</sub>

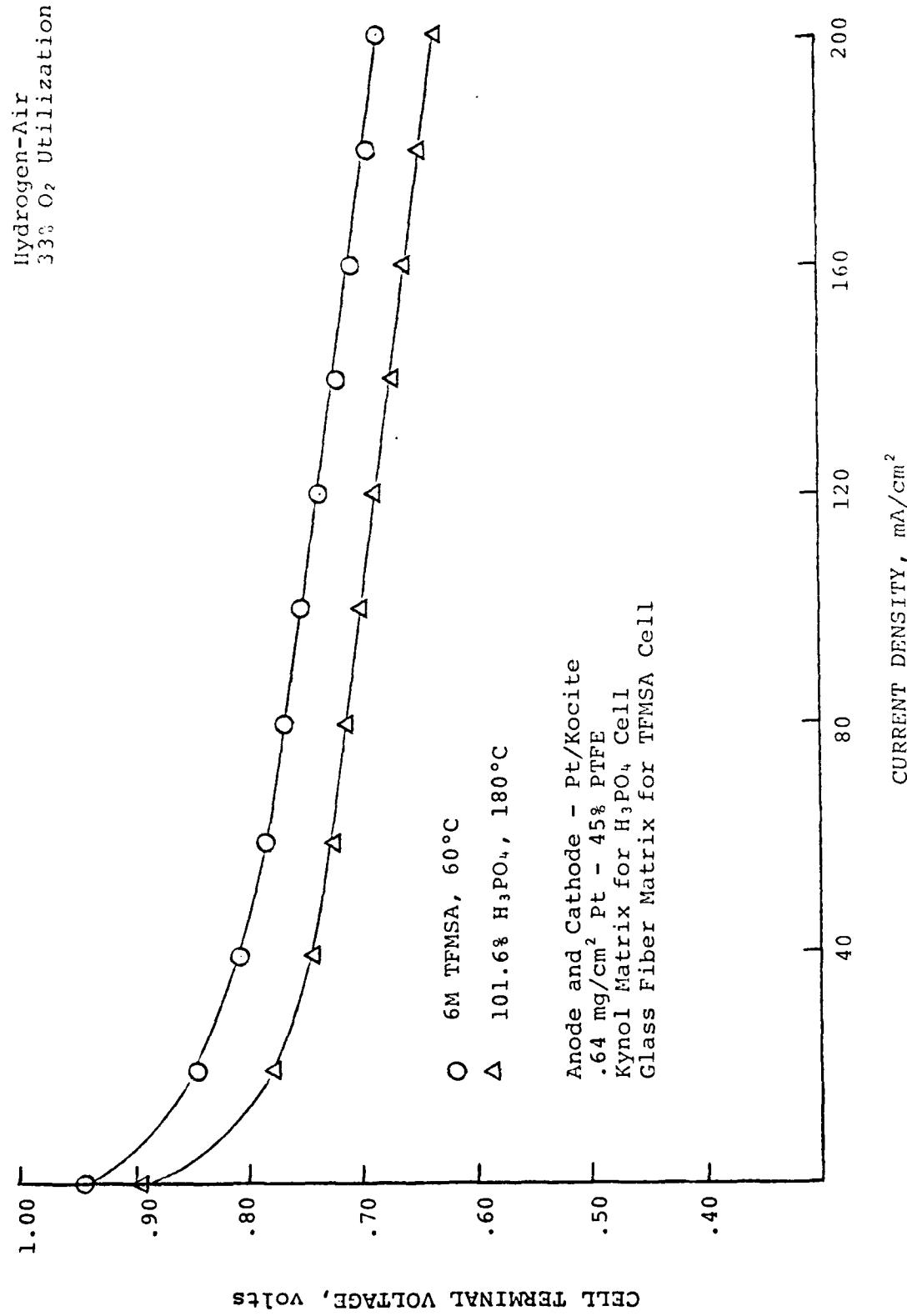


FIGURE 15  
ENDURANCE OF Pt ON KOCITE ELECTRODES

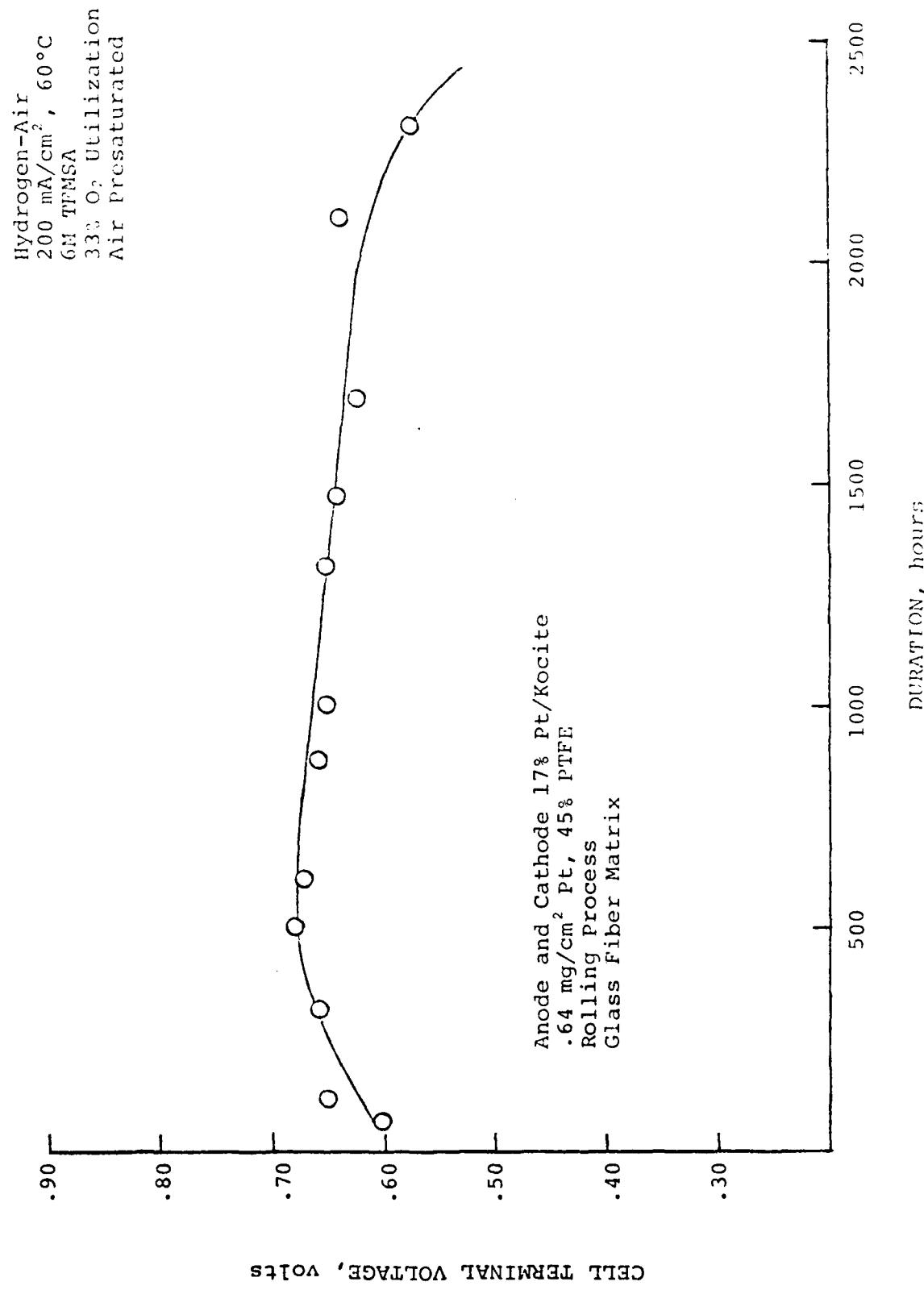


FIGURE 16

## PERFORMANCE OF Pt ON CARBON ELECTRODES

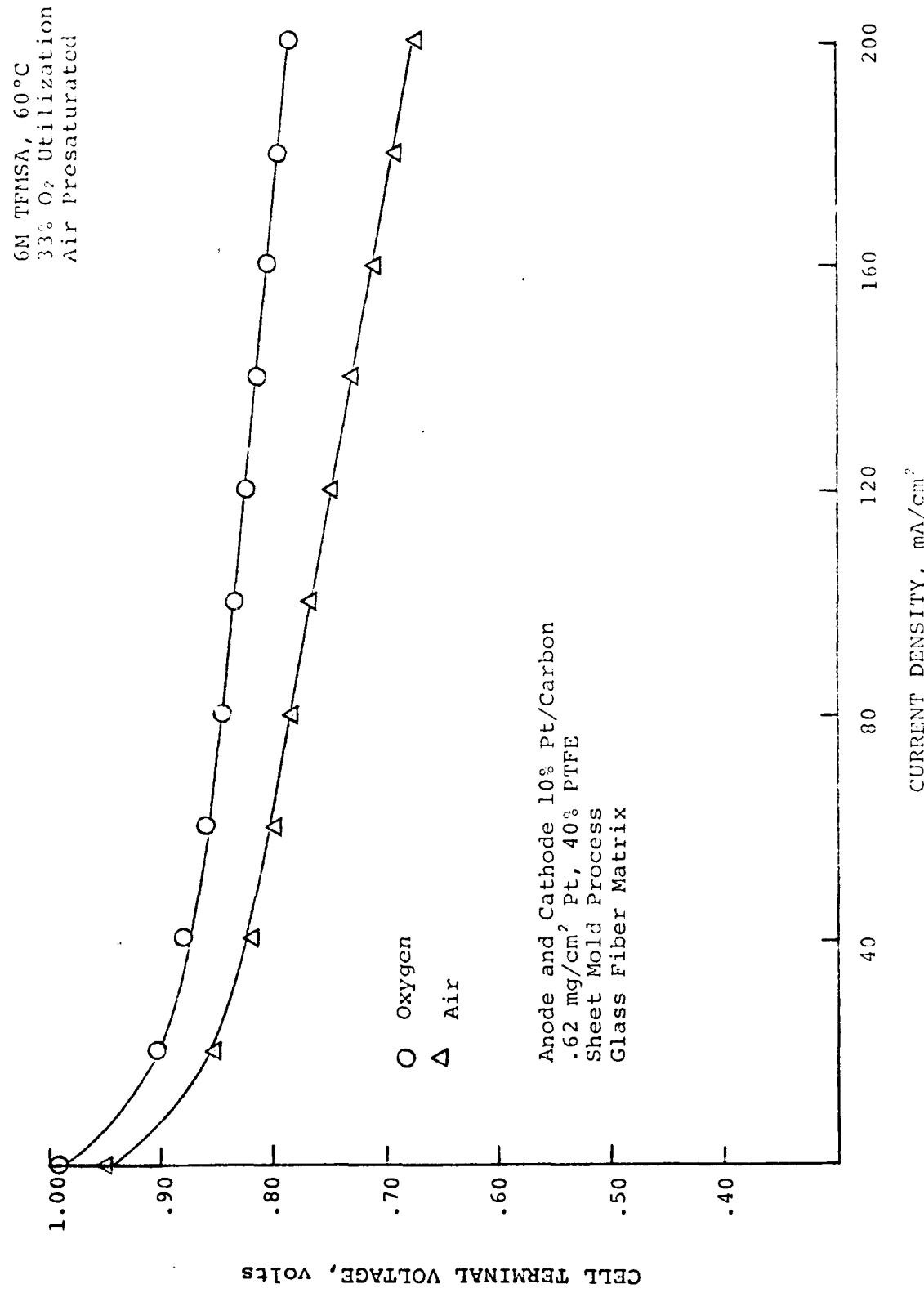
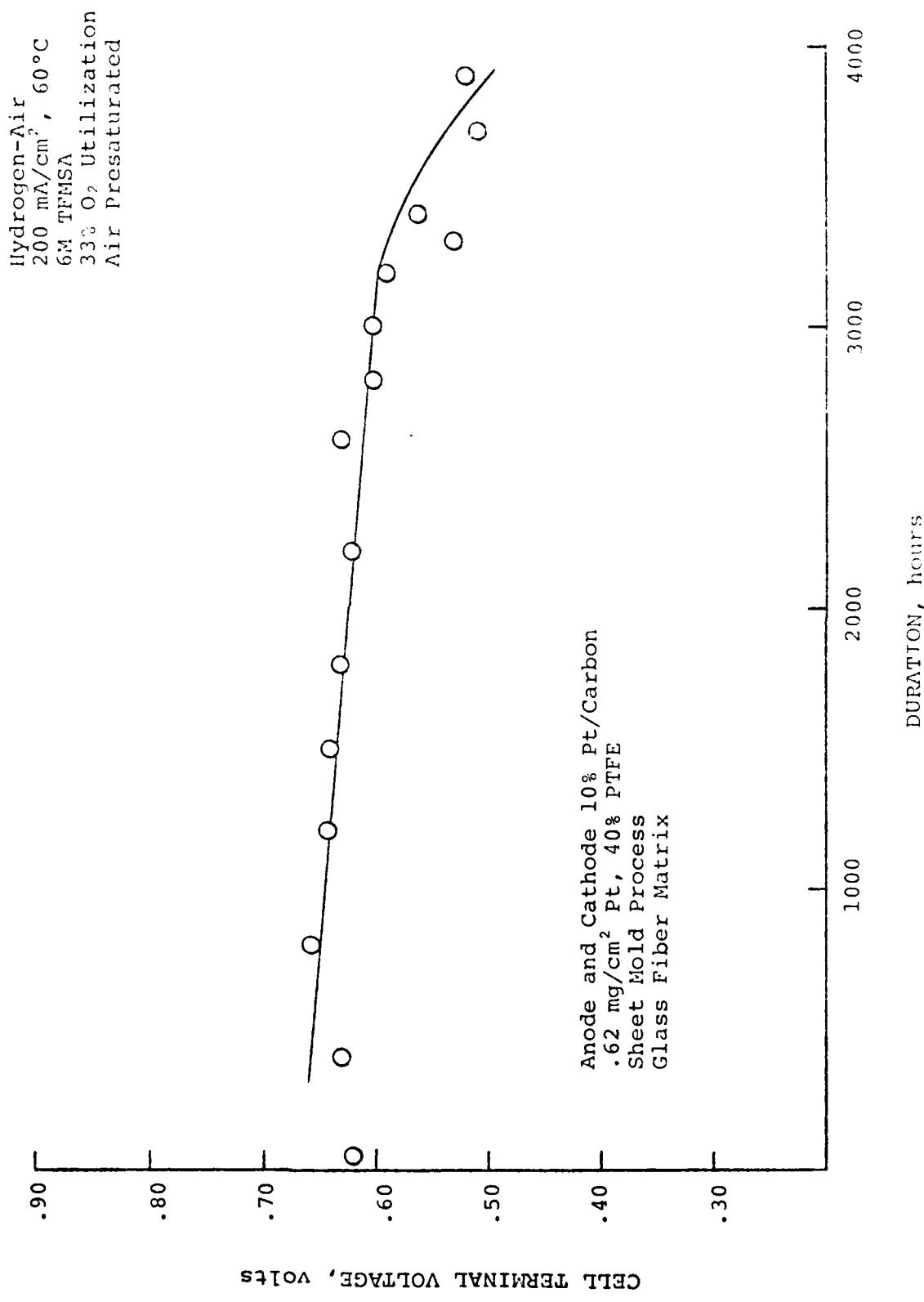


FIGURE 17  
ENDURANCE OF Pt ON CARBON BLACK ELECTRODES



was maintained for at least 3000 hours. Significant performance loss was related to matrix degradation, as evidenced by severe gas crossover and some electrode flooding.

It must be pointed out that, during the endurance testing of TFMSA cells, cell performance fluctuated to a greater degree than is normally experienced with phosphoric acid fuel cells. These fluctuations were probably caused by some temperature cycling during operation, as the cells were not thermostated. In addition, slight acid loss from continually operating cells may have been a factor. Electrolyte replenishment was generally performed at least on a twice a week basis. During endurance testing there was never any evidence of acid decomposition at 60°C nor was there any odor of H<sub>2</sub>S in the effluent gas streams. Hydrogen sulfide, if present, would be expected to readily adsorb to the hydrogen electrode and cause severe anode poisoning losses. All cells during this program appeared to be cathode limited as is the case with most acid fuel cells. Severe anode polarization effects could be induced if the entering hydrogen contained significant amounts of carbon monoxide. Attempts to operate cells with a fuel containing 1% CO resulted in immediate and severe losses of about 250 mV in the cell terminal voltages. Initial cell performance could be restored when pure hydrogen was again supplied.

### 3.0

### CONCLUSIONS

Aqueous solutions in which the mole fraction of TFMSA is less than about .20 have been shown to be effective electrolytes for use in low temperature fuel cells. Use of dilute solutions of triflic acid results in improved kinetics for the air reduction reaction when compared with more conventional electrolytes such as concentrated phosphoric acid. When tested in actual subscale size TFMSA fuel cells, various electrode structures exhibited performance increases at least 50 mV higher than similarly loaded electrodes operating in phosphoric acid at much higher temperatures. A variety of electrocatalysts (such as unsupported Pt and Pt supported on carbon and Kocite) were successfully employed in aqueous TFMSA fuel cells.

Aqueous TFMSA cells could be operated stably at temperatures up to 60°C if the initial acid concentration was maintained. Effective water management during long-term testing was the most important factor relating to cell stability. Cells were tested for up to 3900 hours and a moderate stability was sustained for 3000 hours. The van Laar equations appeared to give a reasonable approximation of the activity coefficients of both TFMSA and water as a function of the solution composition.

ENERGY RESEARCH CORPORATION

The partial pressures of water calculated by the van Laar analysis were utilized to maintain cell water balance. The analysis also predicted that acid loss from operating cells at 60°C with dilute triflic acid electrolyte would not be a major problem. The 6M TFMSA solution appears to be roughly an optimum concentration at 60°C if the entering air to the fuel cell is at ambient temperature. Cell stability was improved when the entering air was humidified.

At the temperatures evaluated during this program, there was no evidence of any acid decomposition. The cells were cathode controlled as no major anode decay mechanisms could be identified when operating with pure hydrogen. When the fuel stream contained 1% CO, immediate anode poisoning was evident and significant cell losses were incurred.

4.0 RECOMMENDATIONS FOR FUTURE WORK

Since excellent performance levels and acceptable endurance capabilities have been demonstrated for subscale aqueous TFMSA fuel cells, future efforts should be directed at scaling up this technology. Attempts should be made to assemble and operate a multi-cell unit (2 to 3 cells) with the individual electrodes having an area of at least 0.5 square feet. It will be important to determine whether water balance can be maintained with this configuration, as the possibility exists for significant temperature differentials within the cell.

A multi-cell unit will also have a tendency to generate significant heat. During continual operation, a TFMSA stack will probably reach temperatures in excess of 60°C. This is dependent on operating current density, stack heat transfer characteristics, air flow rates, and method of cooling. If heat buildup problems are prevalent, the upper temperature limitation of TFMSA cells will have to be identified.

Triflic acid cells tested to date have been susceptible to severe CO poisoning because of the low operating temperatures. At higher temperatures (in the range of 90 to 100°C) the tolerance to poisons should improve. The exact CO concentration levels which can be tolerated must be identified as a function of temperature. Higher temperature operation must also be consistent with acid stability and low acid volatility characteristics.

ENERGY RESEARCH CORPORATION

REFERENCES CITED

1. Adams, A.A. and Foley, R.T., "Research on Electrochemical Energy Conversion Systems," Report No. 2, American Univ. for USA MERADCOM, Contract DAAK02-72-C-0084, Feb. 1973.
2. Adams, A.A. and Foley, R.T., "Research on Electrochemical Energy Conversion Systems," Report No. 5, American Univ. for USA MERADCOM, Contract DAAK02-72-C-0084, July 1974.
3. Foley, R.T., "Present Status of Development of Low Temperature Acid Electrolytes," National Fuel Cell Seminar, Bethesda, MD, June 1979.
4. George, M. and Januszkieicz, S., "New Materials for Fluorosulfonic Acid Electrolyte Fuel Cells," Final Report by ERC for USA MERADCOM, Contract DAAK02-75-C-0045, June 1977.
5. Howells, R.D. and McCown, J.D., Chem. Reviews, 77, pg 71, Feb. 1977.
6. Hughes, V.B., et al, Journ. Applied Electrochem., 7, pg 161, 1977.
7. Kunz, H.R. and Gruver, G.A., Journ. Electrochem. Soc., 122, pg 1279, Oct. 1975.
8. Perry, J.H., Chemical Engineers' Handbook, pg 527, 1950.
9. Sarada, T., Granata, R.D., and Foley, R.T., Journ. Electrochem. Soc., 125, pg 1899, Dec. 1978.
10. 3M Company, Technical Information Bulletin, Trimsylate Acid (FC-24), Oct. 1970.
11. Weast, R.C., Ed., Handbook of Chemistry and Physics, pg D-160. Cleveland, Ohio: CRC Press, 1973.
12. Welsh, L.B. and Leyerle, R.W., "Optimization of Pt-Doped Kocite Electrodes in  $H_3PO_4$  Fuel Cells," Final Report by UOP for USA MERADCCM, Contract DAAG-76-C-0014, May 1979.

DISTRIBUTION LIST

Commander (12)  
Defense Documentation Center  
Cameron Station, Bldg. 5  
ATTN: TISIA  
Alexandria, VA 22314

Chief (1)  
Research, Development & Acquisition  
Office, Deputy Chief of Staff  
Department of the Army  
Washington, DC 20310

Office of the Under Deputy Secretary (1)  
of Defense (Research & Advanced Technology)  
ATTN: ASST DIR, Electronics & Physical  
Sciences  
Washington, DC 20301

Director, Technical Information (1)  
Advanced Research Projects Agency  
1400 Wilson Blvd  
Arlington, VA 22209

Commander (1)  
US Army Materiel Development  
and Readiness Command  
ATTN: DRCDE-D  
5001 Eisenhower Avenue  
Alexandria, VA 22333

Commander (1)  
US Army Tank-Automotive R&D Command  
Technical Library/DRDTA-UL  
Warren, MI 48090

Commander (1)  
US Army Electronics R&D Command  
ATTN: DRSEL-TL-P  
Fort Monmouth, NJ 07703

Commander (1)  
US Army Transportation Research &  
Engineering Command  
ATTN: Research Directorate  
Fort Eustis, VA 23604

Chief (1)  
US Army Security Agency  
Arlington Hall Station  
Arlington, VA 22212

Technical Documents Center (2)  
US Army Mobility Equipment R&D Command  
ATTN: DRDME-WC  
Fort Belvoir, VA 22060

Chief (1)  
Naval Ships Engineering Center  
Department of the Navy  
ATTN: Code 6157D, Mr. Albert Homy  
Washington, DC 20362

Director, Power Branch (1)  
Office of Naval Research  
ATTN: 473  
800 Quincy Street  
Arlington, VA 22217

Department of the Navy (1)  
Office of Naval Research  
Ballston Tower #1  
800 N. Quincy Street Code: 472 Room 624  
Arlington, VA 22217

Commander (1)  
Naval Ordnance Test Station  
China Lake, CA 93555

Commander (1)  
Naval Electronics Laboratory Center  
ATTN: Research Library  
San Diego, CA 92152

Director (1)  
US Naval Research Laboratory  
ATTN: Code 2027  
Washington, DC 20390

Commander (1)  
Aerospace Power Division  
ATTN: AFAPL/PO (Mr. J.D. Reams)  
Wright-Patterson Air Force Base  
Dayton, OH 45443

Commander (1)  
Department of the Air Force (AFSC)  
Rome Air Development Center  
ATTN: RBEG, (Mr. F.J. Mollura)  
Griffiss AFB, NY 13441

Commander (1)  
AFEWC (SURP)  
San Antonio, TX 78241

DISTRIBUTION LIST

Power Information Center (1)  
University City Science Center  
3624 Science Center  
Philadelphia, PA 19104

Director (1)  
George Marshall Space Flight Center  
ATTN: Mr. J.L. Miller (M-ASTR-E)  
Huntsville, AL 38809

Director (1)  
Lewis Research Center  
National Aeronautics & Space Administration  
ATTN: Mr. H.J. Schwartz (M.S. 309-1)  
21000 Brook Park Road  
Cleveland, OH 44135

Dr. Paul Nelson, Director (1)  
Argonne National Laboratory  
Bldg 205  
9700 South Cass Avenue  
Argonne, IL 60439

Mr. Norman Rosenberg (1)  
US Department of Transportation  
Transportation Systems Center  
55 Broadway  
Cambridge, MA 02142

US Department of Energy (1)  
ATTN: Mr. Gary Voelker  
20 Massachusetts Avenue, NW  
Washington, DC 20545

Dr. Paul Milner (1)  
Room 1D-259  
Bell Telephone Laboratories  
Murray Hill, NJ 07974

Electrochimica Corporation (1)  
2485 Charleston Road  
ATTN: Technical Library  
Mountain View, CA 94040

Engelhard Industries Division (1)  
Engelhard Minerals & Chemicals Corp  
Government Services Department  
70 Wood Avenue, South  
Metro Park Plaza  
ATTN: V.A. Forlenza  
Iselin, NJ 08830

Mr. George Ciprios (1)  
Exxon Research & Engineering  
PO Box 8  
Linden, NJ 07036

General Electric Company (1)  
50 Fordham Road  
ATTN: L.J. Nuttall  
Bldg. 1A  
Wilmington, MA 01887

P.L. Howard Associates, Inc (1)  
Millington, MD 21561

Power Systems Division (1)  
United Technologies Corporation  
PO Box 109  
Governor's Highway  
South Windsor, CT 06074

Power Systems Division (1)  
United Technologies Corporation  
ATTN: Dr. H. Russel Kunz  
PO Box 109, Governor's Highway  
South Windsor, CT 06074

Occidental Research Corporation (1)  
ATTN: Herbert P. Silverman  
PO Box 310, Department 2-K  
LaVerne, CA 91750

Union Carbide Corporation (1)  
Parma Research Center  
PO Box 6166  
ATTN: Dr. R. Brodd  
Parma, OH 44101

Energy Research Corporation (1)  
ATTN: Dr. B.S. Baker  
3 Great Pasture Road  
Danbury, CT 06810

Dr. S.B. Brummer (1)  
Director of Physical Research  
EIC, Inc.  
55 Chapel Street  
Newton, MA 02158

Electric Power Research Institute (1)  
ATTN: A.P. Fickett  
PO Box 10412  
Palo Alto, CA 94304

DISTRIBUTION LIST

Dr. Ralph Roberts (1)  
Energy Resources & Environmental Systems  
Engineering  
The MITRE Corporation  
Mail Stop W-389  
Westgate Research Park  
McLean, VA 22101

Universal Oil Products, Inc. (1)  
Ten UOP Plaza  
ATTN: Stephen N. Massie  
Government Contract Administrator  
Des Plains, IL 60016

Technology Center (1)  
ESB Incorporated  
19 W College Avenue  
ATTN: Dr. D.T. Ferrell, Jr.  
Yardley, PA 19067

Dr. Paul Stonehart (1)  
Stonehart Associates, Inc.  
34 Five Fields Road  
Madison, CT 06443

Dr. Jose Giner (1)  
Giner, Inc.  
14 Spring Street  
Waltham, MA 02154

Massachusetts Institute of Technology (1)  
ATTN: Professor H.P. Meissner  
Cambridge, MA 02138

Dr. Douglas N. Bennion (1)  
Energy & Kinetics Department  
School of Engineering & Applied Science  
5532 Boelter Hall  
University of California  
Los Angeles, CA 90024

University of Florida (1)  
Department of Chemical Engineering  
PO Box 3027  
ATTN: Professor R.D Walker  
Gainesville, FL 32601

L.G. Marianowski (1)  
Manager, Energy Conversion & Storage  
Research  
Institute of Gas Technology  
3424 S. State Street  
Chicago, IL 60616

Dr. R.T. Foley (1)  
Chemistry Department  
The American University  
Washington, DC 20016

State University of New York at Buffalo (1)  
ATTN: Professor Stanley Bruckenstein  
Chemistry Department  
Acheson Hall, SUNY/AB  
Buffalo, NY 14214

Hugh J. Barger, Jr. (1)  
Box 2232  
Davidson, NC 28036

END

DATE

FILMED

8 - 80

DTIC